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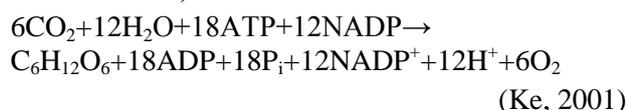
ABSTRACT

In this work, we have added methyl side group (s) on quinone and aromatic ring carbon positions of 1, 4-naphthoquinone (NQ) and on aromatic ring carbon positions of 1, 4-anthraquinone (AQ) in sequential increasing order to check sensitivity of the carbonyl band. In NQ, we observed that the aromatic substitution is more sensitive than the quinonic substitution. In fact, the sequential addition of CH₃ on the quinone ring C₅ and C₆ positions lead into the systematic lowering of the band and such lowering is in average of 5 cm⁻¹ per methyl group. On the other hand, addition on the aromatic ring C₇, C₈, C₉, and C₁₀ positions resulted in mix effect. Indeed, they produce two types of carbonyl band, which are couple and uncouple. For further exploration of the sensitivity of the carbonyl band, we put single or two methyl group (s) on C₇, C₈, C₉, and C₁₀ carbon positions producing four or six NQ model molecules. We concluded that the carbonyl intense bands are more sensitive, split up, to the aromatic ring methyl substitution at C₇ or C₁₀ position. Furthermore, in AQ couple mode of C=O vibration was observed and no splitting of the band was seen on sequential CH₃ addition.

Keywords: Carbonyl band, IR spectra, Naphthoquinone, Anthraquinone, Photosynthesis.

INTRODUCTION

Photosynthesis has special connection with human being, since it is essential for our survival. During this process, carbon dioxide (CO₂) is used up and oxygen (O₂) is evolved as a byproduct (as shown in relation below).



On the other hand, we inhale oxygen (O₂) and exhale carbondioxide (CO₂) (as shown in relation below).



In this ways, waste of one becomes essential usage for other. The photosynthesis process takes away something that is noxious (CO₂) and gives us something precious (O₂) (Ke, 2001). Quinones play vital role to complete the photosynthesis process. Quinone serves as a coupler of electron and proton transfers *in vivo* in energy-transducing membrane for respiration and photosynthesis (Ke, 2001; Patai, 1974; Trumpower, 1982; Okamura *et al.*, 2000).

In photosystem I (PS I) phyloquinone (vitamin K₁), a type of naphthoquinone, occupies A₁ bindingsite. Moreover, Quinone can be used as vitamin, anticancer drugs, and dyes (Ke, 2001; Wakil, 1970; Guin *et al.*, 2011).

Furthermore, in this work we observed normal mode vibrational frequencies of both naphthoquinone and anthraquinone model molecules. The normal modes of vibration (or normal vibration) is defined as a molecular motion in which all the atoms oscillate with the same frequency and pass through their equilibrium positions simultaneously (Banwell *et al.*, 1999).

The N non-linear molecules have, Total normal modes of vibrations=3N-6, Bond-stretching mode=N-1, Bending modes=2N-5. Since molecular vibrational energy differences lies in the infrared region, the infrared (IR) is useful spectroscopy to monitor vibrational energy level in molecules. Specific group of atoms in the molecule absorb at different but definite frequency region (Banwell *et al.*, 1999; Lamichhane, 2011). Here, we have chosen spectra in the region 1800-1550 or 1800-1600 cm⁻¹ because experimentally detectable carbonyl (C=O) and C=C vibrations lie in this region

(Banwell *et al.*, 1999; Coates, 2000; Socrates, 2004; Bellamy, 1980). The set of normal modes of a pure chemical compound in a given environment is unique. For this reason, the IR spectrum, which is representative of the normal mode structure of a molecule, is unique identifier of a specific molecule in a specific environment and provides a “fingerprint” of the molecule (s) (Lamichhane, 2011).

Nonella & Brandli (Nonella *et al.*, 1996) did investigation on methoxy substituted p-benzoquinone. They analyzed 2-methoxy-1, 4-benzoquinone, 2, 3-dimethoxy-1, 4-benzoquinone, 2, 3-dimethoxy-5, 6-dimethyl-1, 4-benzoquinone (MQ_O), 2, 3-dimethoxy-5-methyl-6-phytyl-1, 4-benzoquinone (UQ), 2, 3-dimethoxy-6-allyl-1, 4-benzoquinone by substituting different side groups on quinone ring carbon positions of p-benzoquinone to study whether calculated vibrational spectrum depend on the nature of the substituent. Similarly, Bandaranayake *et al.* (2006) had modified phylloquinone (PhQ) into PhNQ (methyl less PhQ). In addition, Hucke *et al.* determined the binding free energy and charge recombination rate from Q_A⁻ to D⁺(K_{AD}) of 29 different 1, 4-naphthoquinone derivatives with systematically altered structures to study the binding mode of these quinones to the Q_A binding site (Hucke *et al.*, 2002). These researches have inspiration our work.

COMPUTATIONAL METHOD

By using hybrid density functional theory (DFT) method we have done geometrical optimization and

vibrational frequency calculations, employing B3LYP functional and the 6-31G+(d) method within Gaussian 03 (Frisch *et al.*, 2004). All the spectra are generated from the calculated stick spectra by convolving with Gaussian function of wavenumber 4 cm⁻¹ to produce more realistic looking spectra.

RESULTS AND DISCUSSION

In order to check sensitivity of the carbonyl band by sequential substitution of methyl group we have taken two different types of quinones, which are naphthoquinone and anthraquinone. All naphthoquinones have a quinone and an aromatic ring, whereas all anthraquinones contain two aromatic rings and single quinone ring. Hence, for similar side group only feature that distinguish between these two families is an aromatic ring.

Naphthoquinone

Methyl substitution on NQ at quinonic ring carbon positions:

Figure 1 shows structure and numbering of NQ, MNQ and DMNQ. They all belong to class of 1, 4-naphthoquinone family. The MNQ has single methyl group at C₅ positions and the DMNQ has two such groups at C₅ and C₆ positions on the quinone ring. Here, NQ is taken as a reference molecule. The aromatic and quinone ring are presented in all three of them. Going from NQ to MNQ to DMNQ number of the methyl group are in the sequential order of 0, 1 and 2.

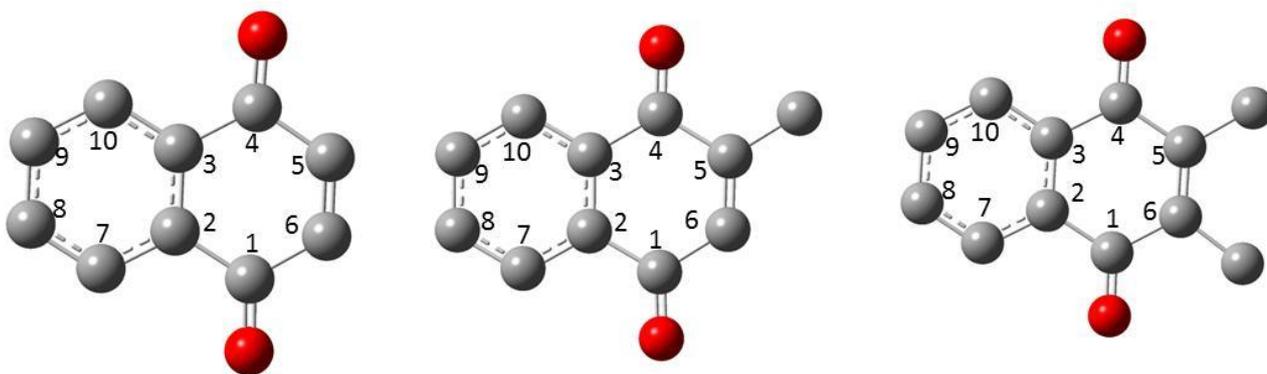


Fig.1. Structure and numbering for 1, 4-naphthoquinone (NQ), 5-methyl-1, 4-naphthoquinone (MNQ), and 5, 6-dimethyl-1, 4-naphthoquinone (DMNQ).

Calculated IR absorption spectra of NQ, MNQ and DMNQ are shown in the figure 2 and their mode assignment is enlisted in Table 1. Here, we have chosen spectra in the region 1800-1550 cm⁻¹

because experimentally detectable carbonyl (C=O) and C=C vibrations lie in this region (Banwell *et al.*, 1999; Coates, 2000; Socrates, 2004; Bellamy, 1980). In the spectra, we have observed three

bands, one intense and two weak. The intense band is produced due to couple carbonyl mode of vibration, whereas the two weaker bands are predominantly due to $C_5=C_6$ stretching and partially double aromatic ring vibration. Actually, the weaker band has at least 82% less intensity than the intense band.

In this paper, our goal is to discuss about effect of methyl substitution on the carbonyl band. Thus, the intense band of NQ/MNQ/DMNQ due to coupled carbonyl modes of vibration was observed at 1735/1730/1721 cm^{-1} . Indeed, the sequential addition of the methyl group resulted into the systematic lowering in the intense band and such lowering was in average of 5 cm^{-1} per methyl group. Importantly, in all three quinones similar nature of carbonyl band (couple) was seen. We know that, the normal mode vibrational frequencies depend

upon the strength of the bond between two atoms and reduced mass of the molecule (Banwell *et al.*, 1999). In fact, how much effect on the charge distribution of the functional group due to the presence of particular side group is reflected upon change in its corresponding frequency? In NQ, electronic charge distribution homogeneously distributed over two $C=O$ modes give rise to couple mode of carbonyl vibration. Similarly, presence of one (in MNQ) or two (in DMNQ) methyl group at C_5 or C_5 and C_6 positions is not sufficient enough to make asymmetric distribution of charge among both $C=O$ groups so that it can split the band. In addition, the quinonic $C_5=C_6$ mixed slightly with symmetric $C=O$ stretching vibration of NQ, MNQ and DMNQ occur at 1671, 1683, and 1670 cm^{-1} respectively and their aromatic partially double $C=C$ mode was seen at single frequency 1640 cm^{-1} .

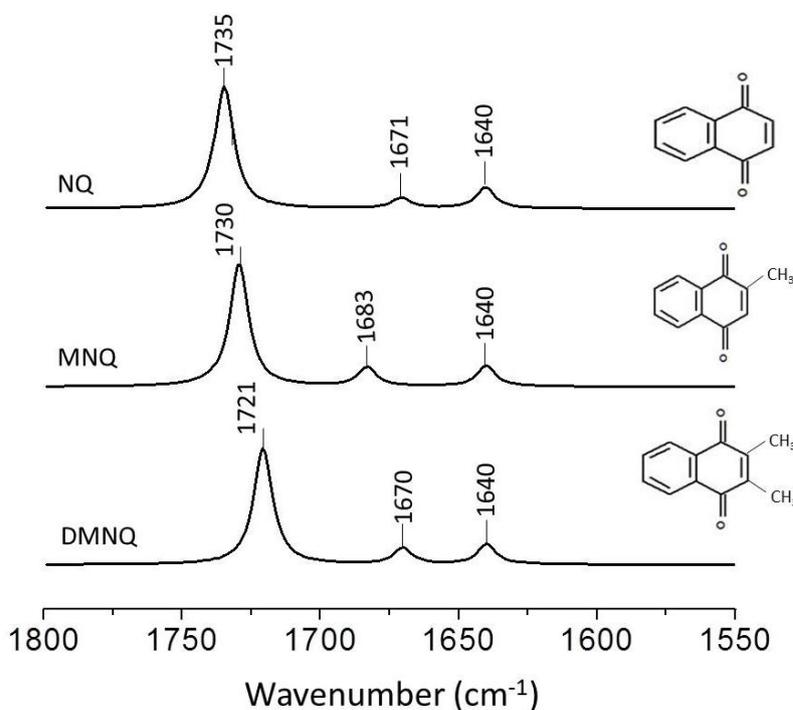


Fig. 2. Calculated IR absorption spectra of NQ, MNQ and DMNQ in gas phase.

Table 1. Mode Assignments (in cm^{-1}) for NQ, MNQ, and DMNQ

Modes	NQ	MNQ	DMNQ
ν ($C=O$), as	1735 (380)	1730 (391)	1721 (372)
ν ($C_5=C_6$), q	1671 (35)	1683 (62)	1670 (52)
ν ($C=C$)*, a	1640 (69)	1640 (68)	1640 (66)

Abbreviations: as, asymmetric; q, quinone ring; *, bond is partially double; a, aromatic ring.

Methyl substitution on NQ at aromatic ring carbon positions:

Figure 3 shows the structure and numbering of five methyl substituted naphthoquinones, which are NQ, NQ₇, NQ_{7,8}, NQ_{7,8,9}, and NQ_{7,8,9,10}. The NQ molecule was taken as a reference molecule and methyl group was added on it in sequential manner as 1, 2, 3, and 4. Naming of the molecules were done according to position and

number of the methyl group. For example, NQ₇ refers to the molecule that has single methyl group at C₇ position. Similarly, NQ_{7,8} refers to the naphthoquinone that has two methyl groups at C₇ and C₈ positions. In fact, the number in the subscript represent position of the methyl group and total count of such number gives total substitution of the group.

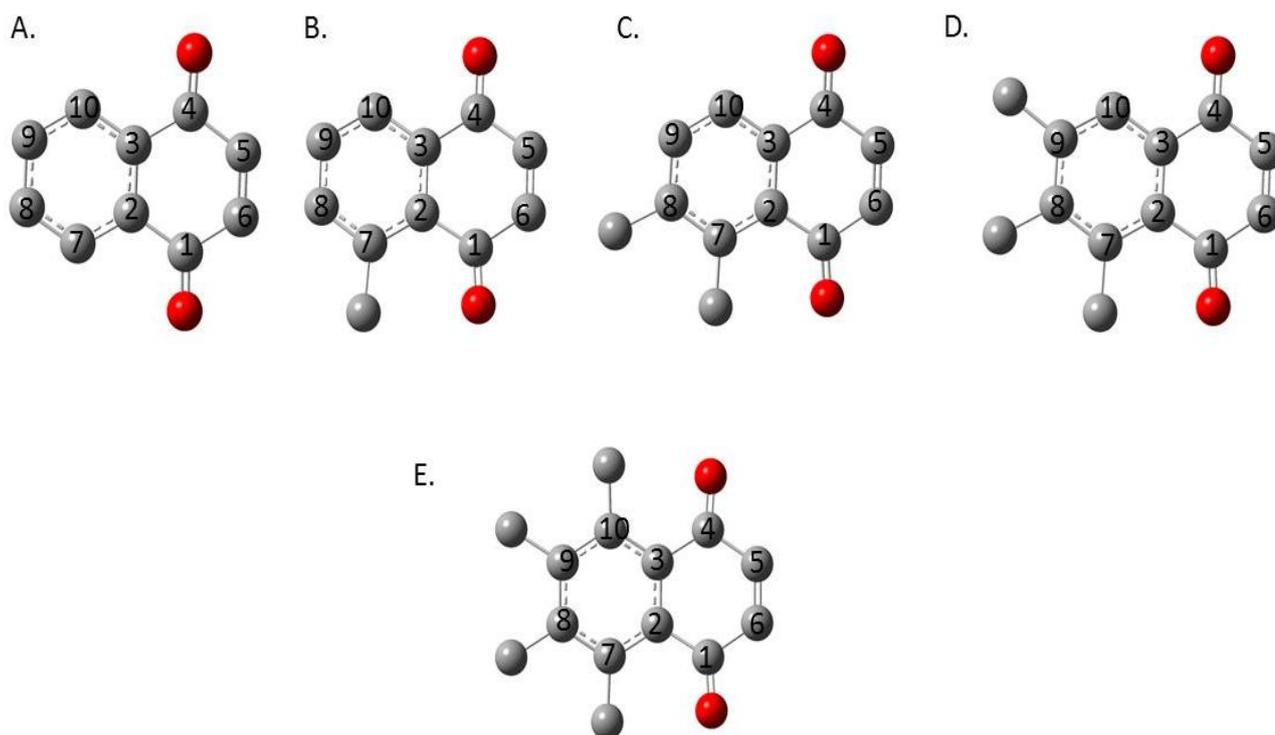


Fig. 3. Structure and numbering for (A) 1, 4-naphthoquinone (NQ), (B) 7-methyl-1, 4-naphthoquinone (NQ₇), (C) 7, 8-dimethyl-1, 4-naphthoquinone (NQ_{7,8}), (D) 7, 8, 9-trimethyl-1, 4-naphthoquinone (NQ_{7,8,9}), and (E) 7, 8, 9, 10-tetramethyl-1, 4-naphthoquinone (NQ_{7,8,9,10}).

Figure 4 shows the calculated IR absorption spectra of five different naphthoquinones (NQ, NQ₇, NQ_{7,8}, NQ_{7,8,9}, and NQ_{7,8,9,10}) and their prominent modes are enlisted in table 2. In the spectra, two different nature of carbonyl band were observed: couple and uncouple. The NQ and NQ_{7,8,9,10} have an intense couple carbonyl band, respectively, at 1735 and 1714 cm⁻¹. On the other hand, the sequential increment of methyl group from C₇, C₈, and C₉ resulted into uncoupling of the band. On such splitting the couple C=O mode separated into C₁=O and C₄=O stretching modes of vibration and were 8 or 9 cm⁻¹ apart. Among C₁=O and C₄=O modes, former one goes to the lower frequency and latter

one remains on the upper frequency. The C₁=O mode not only goes to the lower frequency but its intensity also reduces to one-fourth than C₄=O mode. In fact, C₁=O mode of NQ₇, NQ_{7,8} and NQ_{7,8,9} were found at 1723, 1721, and 1719 cm⁻¹ respectively and their C₄=O mode was found respectively, at 1732, 1729, and 1728cm⁻¹. In addition, the quinonic C₅=C₆ mixed slightly with symmetric C=O stretching vibration of NQ, NQ₇, NQ_{7,8}, NQ_{7,8,9} and NQ_{7,8,9,10} occurred, respectively, at 1671, 1678, 1679, 1678, and 1684 cm⁻¹ and their aromatic partially double C=C mode was seen respectively, at 1640, 1634, 1623, 1624, and 1580 cm⁻¹.

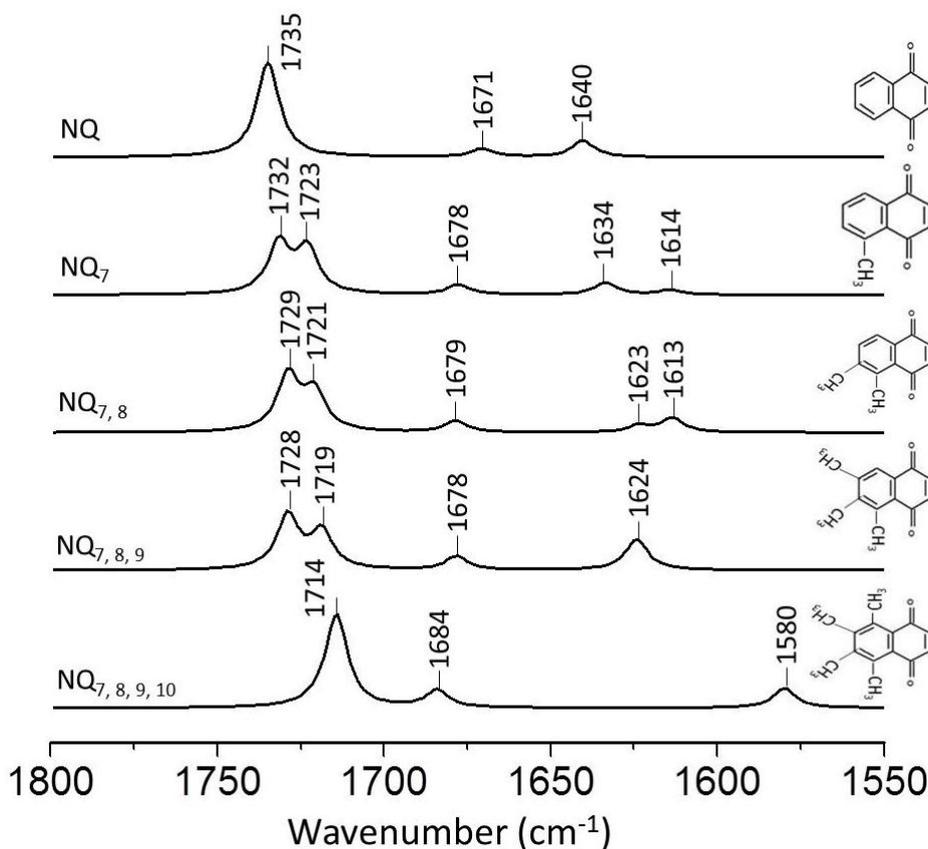


Fig. 4. Calculated IR absorption spectra of NQ, NQ₇, NQ_{7,8}, NQ_{7,8,9}, and NQ_{7,8,9,10} in gas phase.

Table 2. Mode Assignments (in cm⁻¹) for NQ, NQ₇, NQ_{7,8}, NQ_{7,8,9}, and NQ_{7,8,9,10}

Modes	NQ	NQ ₇	NQ _{7,8}	NQ _{7,8,9}	NQ _{7,8,9,10}
v (C=O), as	1735 (380)				1714 (387)
v (C ₁ =O)		1723 (165)	1721 (165)	1719 (160)	
v (C ₄ =O)		1732 (213)	1729 (237)	1728 (227)	
v (C ₅ =C ₆), q	1671 (35)	1678 (41)	1679 (49)	1678 (56)	1684 (72)
v (C=C)*, a	1640 (69)	1634 (50)	1623 (28)	1624 (129)	1580 (82)

Abbreviations: as, asymmetric; q, quinone ring; *, bond is partially double; a, aromatic ring.

Upon sequential substitution of methyl group on aromatic ring, we were able to observe that the carbonyl band is sensitive to the certain substitutions. For deeper understanding, we alternatively added single methyl group at four different carbon positions of the ring. Figure 5

shows the structure and numbering of NQ₇, NQ₈, NQ₉, and NQ₁₀. We gave name of the NQ according to the position of such substitution in the ring. For example, NQ₇ refers to the naphthoquinone that has the methyl group at C₇ position of the aromatic ring.

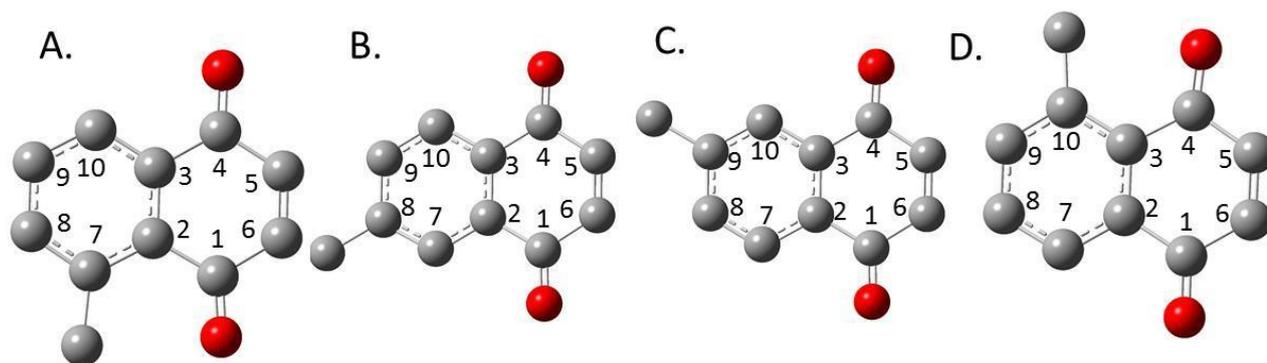


Fig. 5. Structure and numbering for (A) 7-methyl-1, 4-naphthoquinone (NQ₇), (B) 8-methyl-1, 4-naphthoquinone (NQ₈), (C) 9-methyl-1, 4-naphthoquinone (NQ₉), and (D) 10-methyl-1, 4-naphthoquinone (NQ₁₀).

Calculated IR spectra of four different 1, 4-naphthoquinones (NQ₇, NQ₈, NQ₉, and NQ₁₀) is shown in the figure 6. and their mode assignment is enlisted in table 3. Here, NQ₇, NQ₈, NQ₉, and NQ₁₀ have envisioned two different natures of carbonyl bands as shown in Fig. 6: couple and uncouple. In case of NQ₈ & NQ₉, highly active IR band due to coupled C=O vibration was observed at 1734 cm⁻¹. However, in NQ₇ & NQ₁₀ this band split into C₁=O and C₄=O stretching mode of vibration. For NQ₇ C₁=O stretching mode was found at lower frequency (1723 cm⁻¹) having intensity 22% less than C₄=O mode, which occurred at higher frequency (1732 cm⁻¹). In contrast, for NQ₁₀ C₁=O stretching mode remained in the upper frequency (at 1731 cm⁻¹) and C₄=O mode goes down to the lower frequency (at 1723 cm⁻¹) and intensity of former mode was 12% more than the latter.

The normal mode vibrational frequencies depend directly upon the electronic charge distribution. Here, the split carbonyl band charge was non-homogeneously distributed over two C=O bonds compared to that of coupled carbonyl band. Among C₁=O and C₄=O mode, which one goes down on splitting is determined by the position of substituted methyl group. The methyl group affects the charge distribution of nearest neighbor C=O bond pushes the band to lower frequency, while the opposite C=O bond remain undisturbed at upper frequency. In addition, the quinonic C₅=C₆ mixed slightly with symmetric C=O stretching vibration of NQ₈ & NQ₉ occurred at a same frequency 1670 cm⁻¹ and of NQ₇ & NQ₁₀ at 1678 cm⁻¹ and the aromatic partially double C=C mode of NQ₈ and NQ₉/NQ₇ and NQ₁₀ seen at 1647/1634 cm⁻¹.

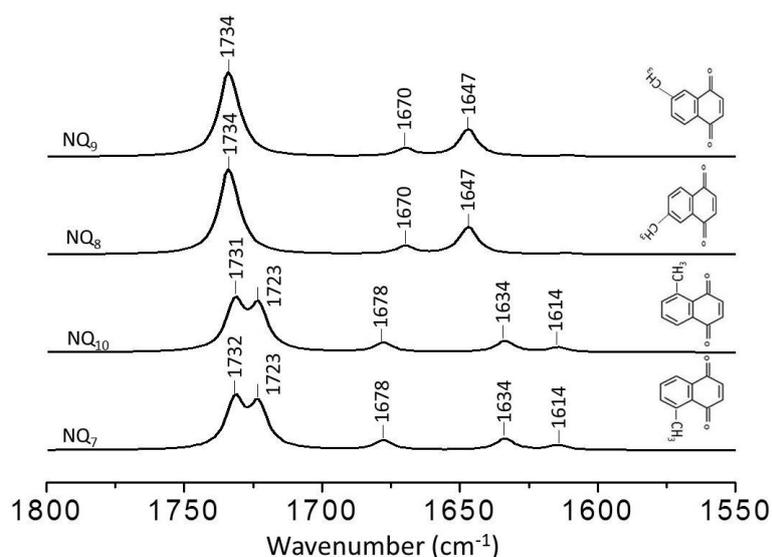


Fig. 6. Calculated IR absorption spectra of NQ₇, NQ₈, NQ₉ and NQ₁₀ in gas phase.

Table 3. Mode Assignments (in cm^{-1}) for NQ_7 , NQ_8 , NQ_9 , and NQ_{10} .

Modes	NQ_7	NQ_8	NQ_9	NQ_{10}
$\nu(\text{C}=\text{O})$, as		1734 (350)	1734 (343)	
$\nu(\text{C}_1=\text{O})$	1723 (165)			1731 (213)
$\nu(\text{C}_4=\text{O})$	1732 (213)			1723 (188)
$\nu(\text{C}_5=\text{C}_6)$, q	1678 (41)	1670 (34)	1670 (34)	1678 (41)
$\nu(\text{C}=\text{C})^*$, a	1634 (50)	1647 (120)	1647 (121)	1634 (51)

Abbreviations: as, asymmetric; q, quinone ring; *, bond is partially double; a, aromatic ring.

For further exploration of sensitivity of the carbonyl band, we have added two methyl groups on C_7 , C_8 , C_9 , and C_{10} positions of NQ obtaining six model molecules. Figure 7 shows their structure and numbering. The number in subscript refers to

the positions of the methyl groups. For example, $\text{NQ}_{7,8}/\text{NQ}_{7,9}/\text{NQ}_{7,10}/\text{NQ}_{8,9}/\text{NQ}_{8,10}/\text{NQ}_{9,10}$ represents NQ that has methyl groups, respectively, at C_7 & C_8/C_7 & C_9/C_7 & C_9/C_7 & C_{10}/C_8 & C_9/C_8 & C_{10}/C_9 & C_{10}/C_9 & C_{10} positions.

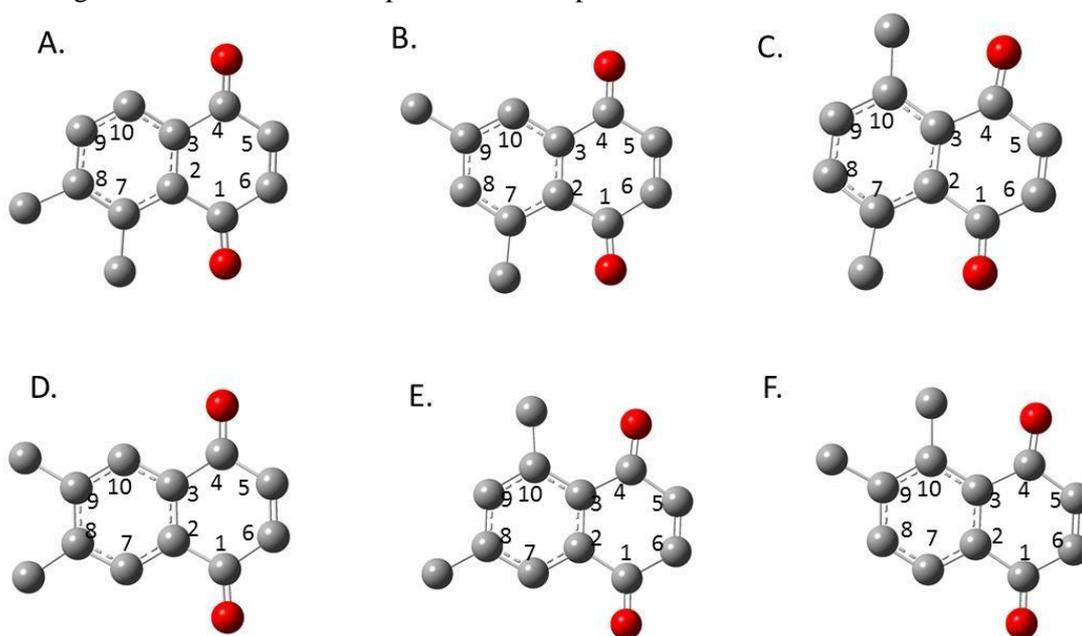


Fig. 7. Structure and numbering for (A) 7, 8-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{7,8}$), (B) 7, 9-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{7,9}$), (C) 7, 10-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{7,10}$), (D) 8, 9-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{8,9}$), (E) 8, 10-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{8,10}$), and (F) 9, 10-dimethyl-1, 4-naphthoquinone ($\text{NQ}_{9,10}$).

Calculated IR spectra of six different 1, 4-naphthoquinones ($\text{NQ}_{7,8}$, $\text{NQ}_{7,9}$, $\text{NQ}_{7,10}$, $\text{NQ}_{8,9}$, $\text{NQ}_{8,10}$, and $\text{NQ}_{9,10}$) is shown in the figure 8. and their mode assignment is enlisted in Table 4. In the spectra, the intense carbonyl band, main focus of this work of $\text{NQ}_{8,9}$ and $\text{NQ}_{7,10}$ are couple, whereas of $\text{NQ}_{7,8}$, $\text{NQ}_{7,9}$, $\text{NQ}_{8,10}$, and $\text{NQ}_{9,10}$ are uncouple. It further strengthened our conclusion that addition of CH_3 group to the C_8 and C_9 positions of the aromatic ring have insignificant effect on the $\text{C}=\text{O}$ band so that it can split the band. However, addition of two

methyl groups, one on C_8 or C_9 position and other on C_7 or C_{10} position of the aromatic ring has prominent effect on the band. In fact, such substitutions lead to breaking up of the band. Most importantly, presence of methyl groups simultaneously at C_7 and C_{10} positions pushes the band down without its uncoupling. The reason behind it is that the presence of the CH_3 groups was unable to bring enough asymmetry on charge among two groups to break the band up and hence lowering down to the same lower frequency was seen.

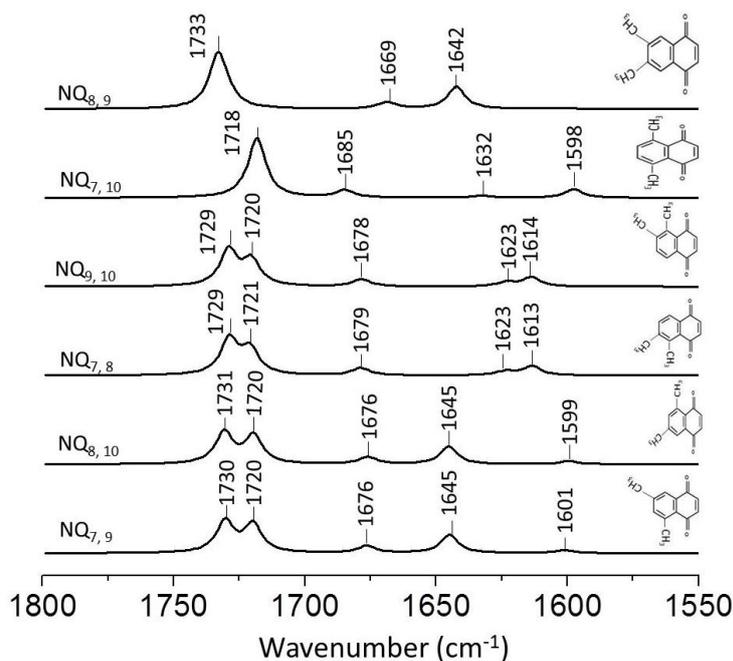


Fig. 8. Calculated IR absorption spectra of $NQ_{7,8}$, $NQ_{7,9}$, $NQ_{7,10}$, $NQ_{8,9}$, $NQ_{8,10}$, and $NQ_{9,10}$ in gas phase.

Table 4. Mode Assignments (in cm^{-1}) for $NQ_{7,8}$, $NQ_{7,9}$, $NQ_{7,10}$, $NQ_{8,9}$, $NQ_{8,10}$, and $NQ_{9,10}$.

Modes	$NQ_{7,8}$	$NQ_{7,9}$	$NQ_{7,10}$	$NQ_{8,9}$	$NQ_{8,10}$	$NQ_{9,10}$
$\nu(\text{C}=\text{O})$, as			1718 (389)	1733 (358)		
$\nu(\text{C}_1=\text{O})$	1721 (165)	1720 (186)			1731 (208)	1729 (236)
$\nu(\text{C}_4=\text{O})$	1729 (237)	1730 (206)			1720 (183)	1720 (165)
$\nu(\text{C}_5=\text{C}_6)$, q	1679 (49)	1676 (46)	1685 (49)	1669 (43)	1676 (46)	1678 (48)
$\nu(\text{C}=\text{C})^*$, a	1623 (28)	1645 (118)	1632 (13)	1642 (144)	1645 (114)	1623 (28)

Abbreviations: as, asymmetric; q, quinone ring; *, bond is partially double; a, aromatic ring Anthraquinone.

Figure 9 shows the structure and numbering scheme for 1, 4-anthraquinone (AQ) family (AQ, AQ_{11} and

$AQ_{11,12}$). Each of them has two aromatic and a quinone ring and differ only by side group/groups.

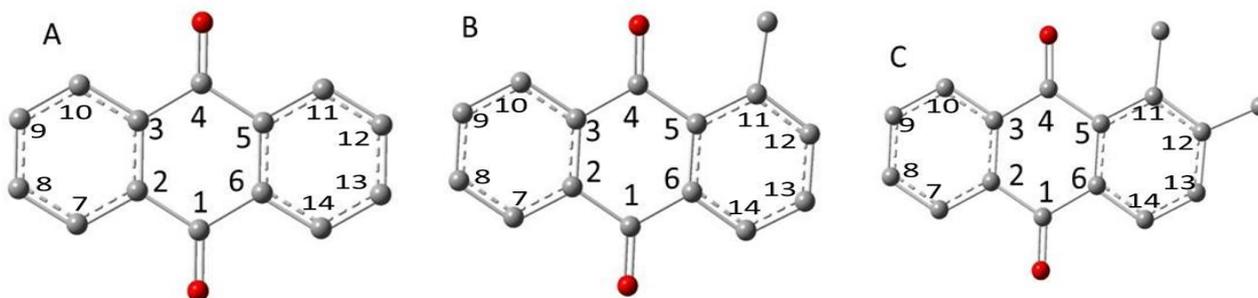


Fig. 9. Structure and numbering for (A) 1, 4-anthraquinone (AQ), (B) 11-methyl-1, 4-anthraquinone (AQ_{11}), (C) 11, 12-dimethyl-1, 4-anthraquinone ($AQ_{11,12}$).

Calculated IR spectra of three different 1, 4-anthraquinones (AQ, AQ₁₁ and AQ_{11,12}) is shown in the Fig. 10. The sequential addition of methyl group on AQ, although leads to the lowering in frequency, has no splitting effect on the intense carbonyl mode of vibration. Such substitution on AQ to get AQ₁₁ and AQ_{11,12} lower down frequency of the intense band respectively by 6 and 8 cm⁻¹. In AQ, highly intense band was observed at 1736 cm⁻¹ and cause of this frequency is due to asymmetric C=O vibration (Fig. 10.). Besides, weak band at 1637 cm⁻¹ was envisioned and was due to vibration of both aromatic ring mixed with little asymmetric C=O vibration. In case of AQ₁₁, highly intense band is observed at 1730 cm⁻¹ which is due to asymmetric C=O vibration. In this case, however, weak band is not like that in AQ, single and easily distinguishable, rather than four weak bands almost of same intensity. The band at 1614/1641 cm⁻¹ is

due to vibration of aromatic ring with/without methyl group. In contrast, aromatic ring without methyl group vibrate together with C₄=O to produce frequency at 1626 cm⁻¹ but aromatic ring with methyl group vibrate with C₁=O to produce it at 1634 cm⁻¹, in both case vibration of aromatic ring is predominant. Hence, we can conclude that addition of methyl group shows direct effect in the weak band. Due to addition of methyl side group, vibration of both aromatic ring is not as homogeneous as AQ but at different frequency, with one predominant than other and mixed with one of the C=O mode.

Moreover, in AQ_{11,12} highly intense band was observed at 1728 cm⁻¹ and cause of this is similar as other two anthraquinones. A vibration of aromatic ring with/without methyl group produced frequency at 1612/1641 cm⁻¹ and due to vibration of both aromatic rings a band was produced at 1623 cm⁻¹.

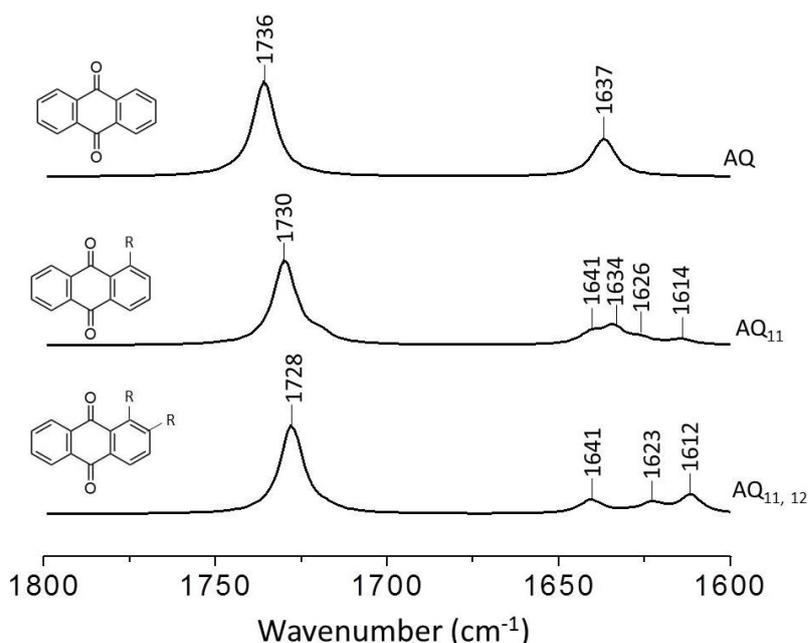


Fig. 10. Calculated IR absorption spectra of AQ, AQ₁₁ and AQ_{11,12} in gas phase.

CONCLUSION

On sequential addition of methyl group (s) to the different carbon positions of naphtho- and anthraquinones model molecules, we concluded that, in NQs, the CH₃ substitution on NQ's quinone ring carbon positions to produce MNQ and DMN, has shown single intense carbonyl band and cause of this band is due to asymmetric carbonyl mode of vibration. Importantly, presence of one methyl

group lowers down frequency (in average) of the band by 5 cm⁻¹. However, such addition on the aromatic ring results into mix effect. On this particular ring substitution, two types of carbonyl bands, which are couple and uncouple, were observed. For the further exploration of splitting effect in the carbonyl band, we added one or two methyl group (s) on C₇, C₈, C₉, and C₁₀ positions of NQ obtaining four or six model molecules. From

this we figured out that C₇ and C₁₀ substitutions are more sensitive to the C=O mode i.e. it leads to the breaking the intense band up into C₁=O and C₄=O stretching mode. Furthermore, the sequential addition of methyl group on AQ, although leads to the lowering in frequency, has no splitting effect on the intense carbonyl mode of vibration. Such substitution on AQ to get AQ₁₁ and AQ_{11, 12} lower down frequency of the intense band respectively by 6 and 8 cm⁻¹.

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