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Effect of additional side groups on the vibrational frequencies of benzoquinone molecules

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Abstract

The present work enumerates detailed computational investigation into the IR spectra in gas phase and in solvent of 1, 4- Benzoquinone family (benzoquinone (BQ), duroquinone (DQ), plastoquinone (PQ), ubiquinone (UQ), and dimethoxy dimethyl benzoquinone (MQo)). In the spectra of BQ, PQ, and DQ, we observed separate intense carbonyl (C=O) and C=C bands respectively around 1730 cm^{-1} (intense), 1645 cm^{-1} (weak). On the other hand, for UQ and MQo, three prominent bands around 1652, 1703, and 1733 cm^{-1} were observed, where two C=O modes were uncoupled but one of the carbonyl is strongly coupled with C=C vibrations. The additional methyl groups downshift the intense carbonyl bands and upshift C=C mode frequencies. The carbonyl modes further downshifted in the solvent phase calculation.

Keywords: Photosynthesis; Reaction center; Benzoquinone; IR spectra; Q_A , Q_B

1. Introduction

Quinone serves as a coupler of electron and proton transfers *in vivo* in energy-transducing membrane for respiration and photosynthesis [1-4]. Based on nature of work, not on types, quinones in the reaction center (RC) are classified as Q_A (primary quinone) and Q_B (secondary quinone). They can be chemically identical or different depending upon RC. For example, ubiquinone in *Rb. sphaeroids* and menaquinone in *Cf. aurantiacus* RC works as both Q_A and Q_B , in contrast in *Chromatium* or *Rp. viridis* RC menaquinone is Q_A and ubiquinone is Q_B . However, each of them has to complete significantly different task. Here, Q_A works as transporter of electron and undergoes only single redox steps, while Q_B works like recipient and has to go through two redox steps. Indeed, their mutual working leads to the proton-coupled electron transport reaction. The former can transport an electron to latter at a time until it gets two

electrons. Eventually after receiving two electrons, Q_B gets two protons from protein membrane forming Q_BH_2 i.e. quinol which then leaves the reaction center.



Q_BH_2 leaves the binding site and a new Q_B occupies the vacant space. The quinol (Q_BH_2) releases two hydrogen atoms whenever it reaches the place of higher redox potential [3]. Thus, this process creates a potential gradient across the photosynthetic membrane which drives ATP synthesis reaction [3]. Moreover, in purple bacteria RC, the electron transfer from Q_A to Q_B spans a distance of 15 Å (edge to edge) and are linked by H-bonds through a His- Fe^{2+} -His complex [4]. On the other hand, the process of proton and electron transfer by a quinone is in reverse direction in respiration to that of photosynthesis [3]. Hence, study of quinones is so important for the understanding of reaction center and eventually about photosynthesis and respiration, which is essential for the survival of living things.

2. Materials and Methods

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) basis within Gaussian 03 [5]. The solvent phase calculation employs IEFPCM method in carbon tetrachloride (CCl_4) solvent.

3. Results and Discussions

1, 4-Benzoquinone Family

Here, we have studied IR spectra and solvent effect of 1, 4-Benzoquinone family by dividing it into the two classes, which are Benzoquinone with and without methoxy side group.

a. Benzoquinone without Methoxy Side Group

i. Structure and Numbering of BQ, PQ, and DQ

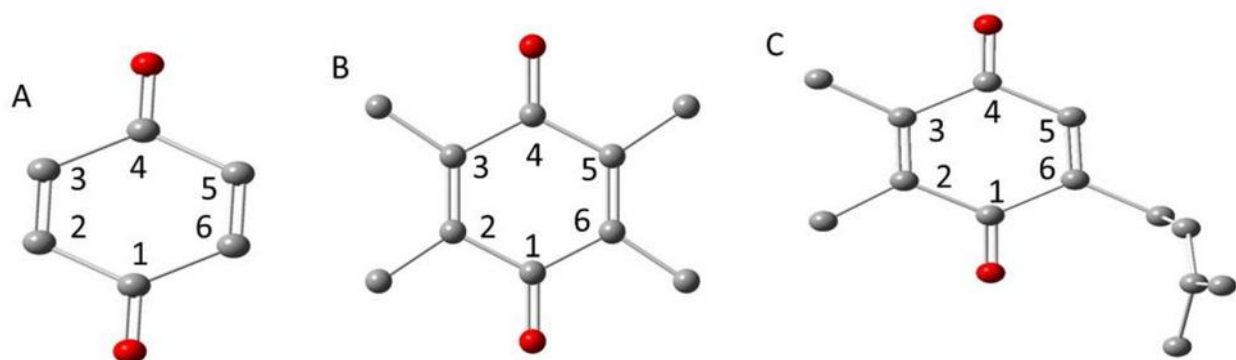


Fig. 1: Structure and numbering for (A) Benzoquinone (BQ), (B) Duroquinone (DQ), (C) plastoquinone (PQ). For the sake of simplicity the hydrogen atoms have been removed.

Figure (1) shows structure and numbering scheme for benzoquinone without methoxy side groups (BQ, PQ, and DQ). They have a quinone ring and differ from one another by particular functional group. Out of three, benzoquinone (BQ) has simplest structure and by replacing all of its hydrogen atom by methyl side group we can get duroquinone (DQ). Similarly, by replacing hydrogen atoms at the positions C₂ and C₃ by methyl groups and at C₆ by isoprene unit we can get plastoquinone (PQ). The information of functional groups is summarized in table (1).

Table 1: Summary side groups in BQ, PQ, and DQ.

1, 4-BQ	Side Groups			
	C ₂	C ₃	C ₅	C ₆
BQ	H	H	H	H
DQ	CH ₃	CH ₃	CH ₃	CH ₃
PQ	CH ₃	CH ₃	H	Isoprene Unit

ii. The IR Spectra of BQ, PQ, and DQ

Calculated IR spectra of BQ, DQ, and PQ are shown in the figure (2) and (3). Figure (2) shows these three quinones and their corresponding spectra. On the other hand, figure (3) shows comparative spectra of all three of them. We have chosen spectra in the region 1800-1600 cm⁻¹ because experimentally detectable carbonyl (C=O) and C=C vibrations lie in this region. From figure (2) we observed that, in the IR spectra respectively of BQ/DQ/PQ, the weak band is at 1651/1675/1663 cm⁻¹ and are due to an out-of-phase vibration of the C=C_r groups (C₂=C₃ and C₅=C₆) of the quinone ring. Given the antisymmetric nature of vibration it is very weakly Raman Active (data not included). In addition to that, a highly intense IR band respectively of them is found at 1735/1707/1714 cm⁻¹ and are due to out-of-phase C=O vibration. These modes also have asymmetric nature of vibration again they have weak Raman activities. Although not always true, as a general rule, band that are weak in Raman spectra are often strong in IR spectra [6].

By analyzing figure (3), we can conclude that BQ, DQ, and PQ have similar nature of spectra. Indeed, all of them have one intense and one weak band. Which means, addition of methyl and isoprene side group, respectively, in BQ to get DQ and PQ does not really change the nature of the spectra. However, addition of methyl side groups lowered the band positions carbonyl vibrations in proportion to the number of methyl groups.

iii. The Solvent Effect

Table (2) shows bond length of carbonyl group and C=C_r (C₂=C₃ and C₅=C₆) of optimized quinone structure in gas phase and CCl₄. The 1AIJ crystal structure [7] indicates that the C₁=O bond is marginally longer than the C₄=O bond (1.234 versus 1.232 Å). The C₁=O and C₄=O bond length of BQ, DQ, and PQ were found shorter in the gas phase than that of the corresponding length in the CCl₄. Among all three, BQ got maximum elongation (0.003 Å) in both C₁=O and C₄=O bond in solvent phase calculation. In

opposite, they got minimum elongation (0.001 Å) in case of PQ. This change in length is due to increase in value of dielectric constant.

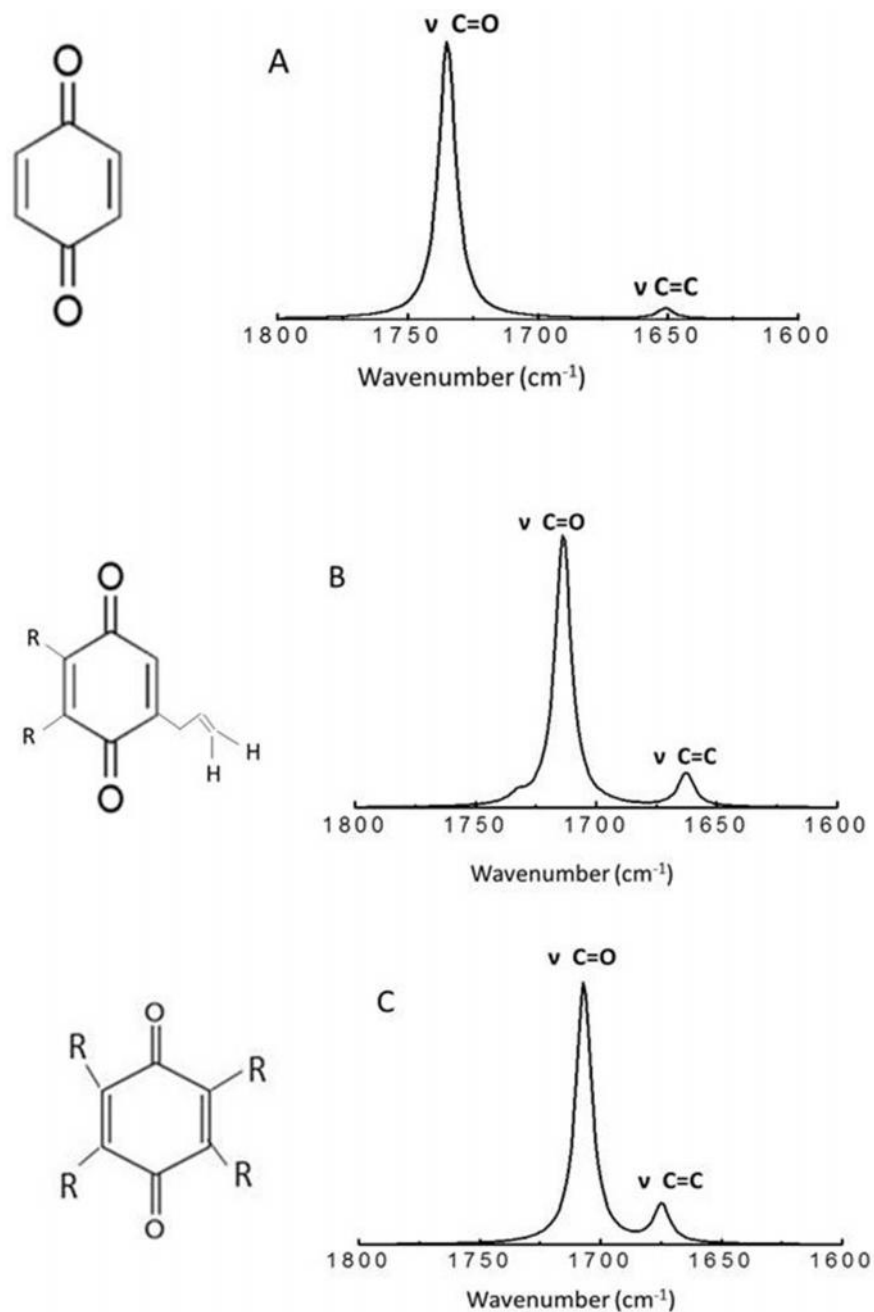


Fig. 2: Structure and gas phase calculated IR spectra in the C=O and C=C vibrating region for the (A) Benzoquinone, (B) Plastoquinone, and (C) Duroquinone. For the sake of simplicity R is written instead of CH₃.

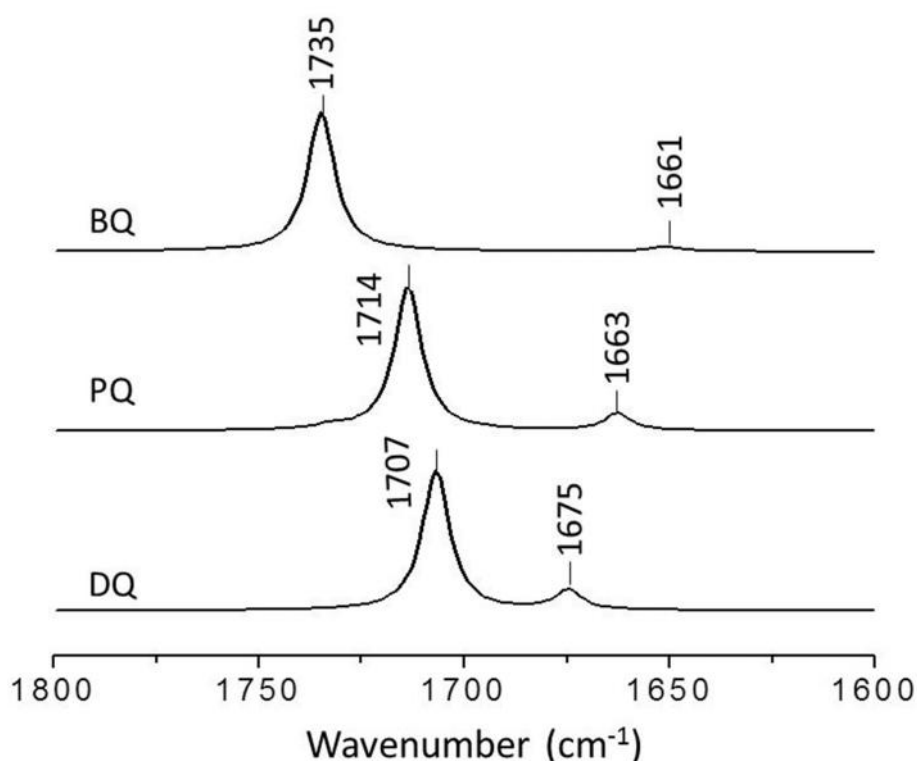


Fig. 3: Calculated IR absorption spectra of BQ, DQ, and PQ in gas phase. The spectra are generated from the calculated stick spectra by convolving with Gaussian function of wavenumber 4 cm^{-1} .

Furthermore, 1AIJ crystal structure [7] indicates that the $\text{C}_2=\text{C}_3$ bond is shorter than the $\text{C}_5=\text{C}_6$ Bond (1.404 versus 1.419 \AA). In contrast, for the case of BQ, DQ, and PQ, in both CCl_4 and gas phase calculation $\text{C}_2=\text{C}_3$ and $\text{C}_5=\text{C}_6$ are equal. Since, in the gas phase or in CCl_4 there is no effect of hydrogen bonding but in the protein environment i.e. in the crystal structure there is effect of hydrogen atom neighbor molecules which is difference of the bond length observed here with the bond length $\text{C}=\text{C}$ and $\text{C}=\text{O}$ group in crystal structure.

So, it can be concluded that calculation of quinone in solvent does effect in carbonyl group but effect is almost negligible for $\text{C}=\text{C}$ bond of quinone ring. Which suggested that the solvent not much constrain the quinone ring.

Table 2: Bond length of carbonyl group and $\text{C}=\text{C}_r$ in (\AA) unit of optimized structure of BQ, DQ, and PQ in Gas Phase (GP), CCl_4 , and Crystal Structure (CS).

Types	$\text{C}_1=\text{O}$			$\text{C}_4=\text{O}$			$\text{C}_2=\text{C}_3$			$\text{C}_5=\text{C}_6$		
	GP	CCl_4	CS	GP	CCl_4	CS	GP	CCl_4	CS	GP	CCl_4	CS
BQ	1.227	1.230	1.234	1.227	1.230	1.232	1.345	1.345	1.404	1.345	1.345	1.419
DQ	1.230	1.232	1.234	1.230	1.232	1.232	1.356	1.356	1.404	1.356	1.356	1.419
PQ	1.229	1.230	1.234	1.230	1.233	1.232	1.358	1.358	1.404	1.347	1.347	1.419

Figure (4) shows comparative IR spectra of BQ, DQ, and PQ in gas phase and CCl₄. From the figure it is obvious that frequency decreases in solvent (CCl₄) than that of in the gas phase calculation. In fact, there is general trend of lowering of frequency in intense band but case is not true for weak band. The cause of the intense band is due to asymmetric C=O vibration, while that of weak band is due to asymmetric C=C_r, C₂=C₃ and C₅=C₆, vibration. The force constant is inversely proportional to the bond length and directly proportional to the frequency i.e. frequency (f) ∝ force constant (k) ∝ {1/ bond length (l)} [8]. Thus, increase in bond length in C₁=O and C₄=O that calculated in solvent than in gas phase results decrease in frequency for intense band {figure (4) and table (2)}. Our results also indicate frequencies shift and bond lengths shift are inversely proportional under calculation in solvent than in gas phase.

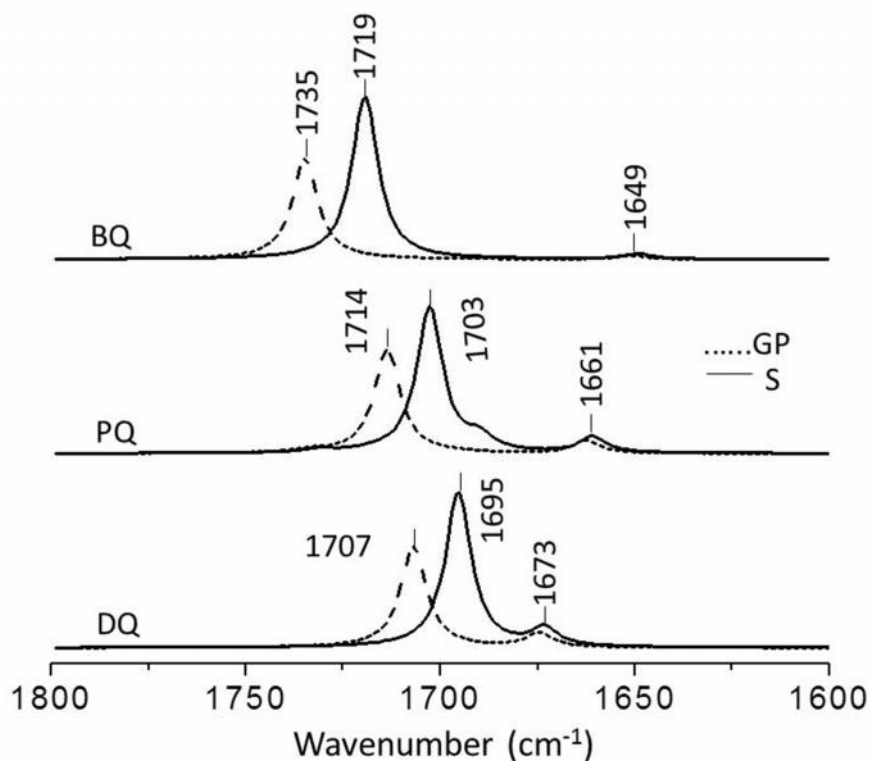


Fig. 4: Comparative spectra of BQ, DQ, and PQ in gas phase and CCl₄. The Spectra are generated from the calculated stick spectra by convolving with Gaussian function of wavenumber 4 cm⁻¹.

b. Benzoquinone with Methoxy Side Group

i. Structure and Numbering of UQ and MQ₀

The structure and numbering scheme for benzoquinone with methoxy side group (MQ₀ and UQ) is shown in figure (5). Both of them have methoxy group at C₂ and C₃ and methyl at C₅. The key component that distinguishes both of them is the functional group at C₅. UQ has isoprene unit at that position, while MQ₀ has methyl side group.

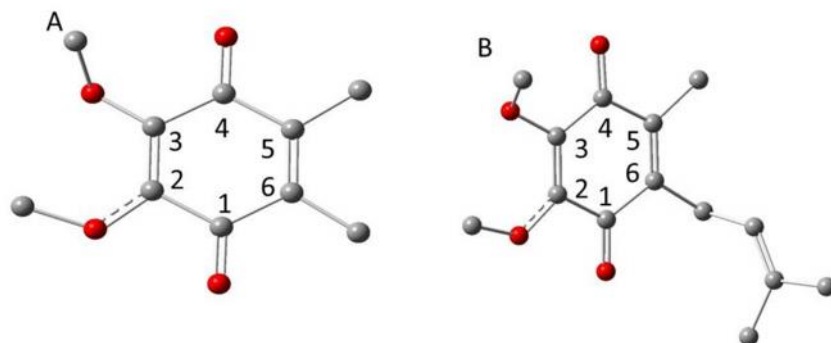


Fig. 5: Structure and numbering for (A) 2, 3-dimethoxy-5, 6-dimethyl benzoquinone (MQ_O) and (B) Ubiquinone (UQ). For the sake of simplicity the hydrogen atoms have been removed.

ii. The IR Spectra of UQ and MQ_O

Here, IR spectra of two methoxy containing benzoquinones (MQ_O and UQ) are shown in figure (6) and (7) in the region of 1800-1600 cm⁻¹. Actually, figure (6) shows structure of MQ_O and UQ and their corresponding IR spectra with different modes of vibration. On the other hand, figure (7) shows the comparative spectra between them.

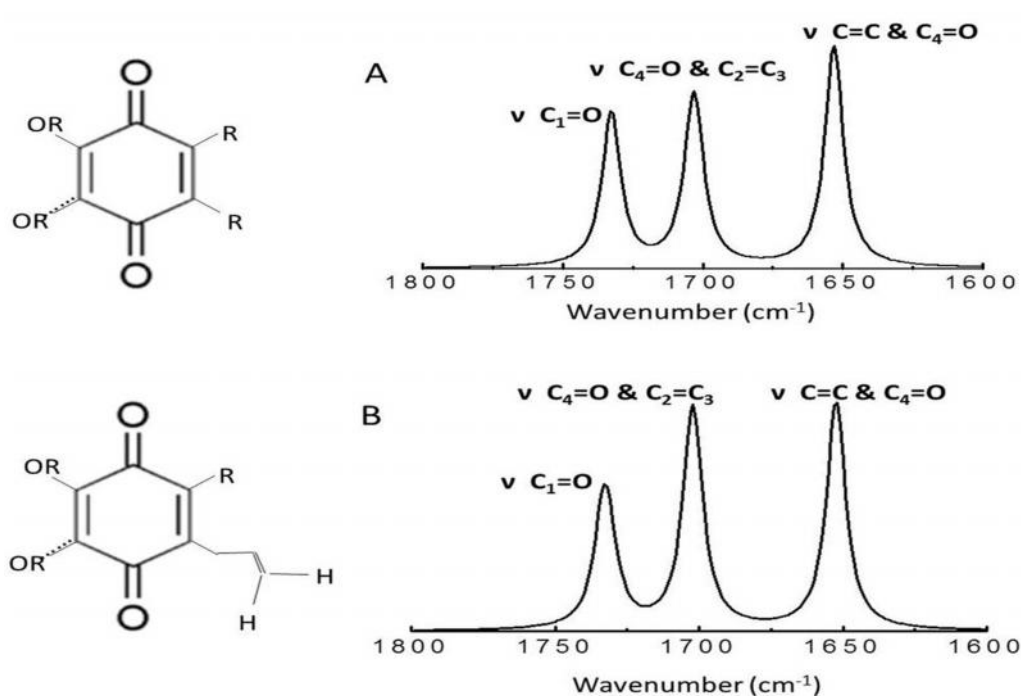


Fig. 6: Structure and gas phase calculated IR spectra in the uncoupled and coupled C–O and C–C vibrating region for the (A) MQ_O and (B) UQ. For the sake of simplicity R is written instead of CH₃.

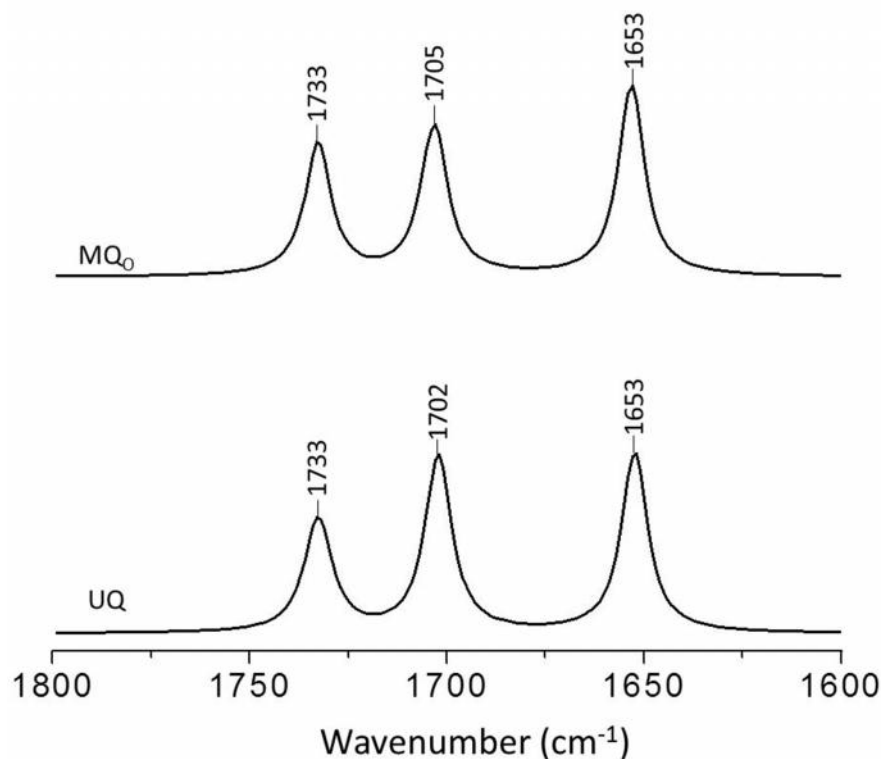


Fig. 7: Calculated IR absorption spectra of UQ and MQ₀ in gas phase. The spectra are generated from the calculated stick spectra by convolving with Gaussian function of wavenumber 4 cm⁻¹.

The IR spectra of UQ and MQ₀ had shown three prominent bands in the 1800-1600 cm⁻¹ region. For both quinones (UQ/MQ₀) bands are observed, respectively, at 1652/1653, 1702/1705, and 1733/1733 cm⁻¹. The first two bands are occurred due to coupled vibration, whereas cause of the last band is due to single mode vibration. In fact, band at 1652/1653 cm⁻¹ of UQ/ MQ₀ are predominantly due to antisymmetric C=C_r (C₂=C₃ and C₅=C₆) vibration coupled to the C₄=O vibration and band at 1702/1705 cm⁻¹ is predominantly due to C₄=O vibration mixed with C₂=C₃ vibration. However, uncoupled C₁=O vibration produced band at 1733 cm⁻¹ for both of them. In MQ₀ presence of two methyl side groups contributed more to the band at 1653 cm⁻¹ and hence it is more intense. But, in UQ due to single methyl side group the intensity of bands at 1653 and 1702 cm⁻¹ are same. The observation of UQ is in closer agreement with the work done by Lamichhane and Hastings [9].

In figure (7), we observed the similar nature of spectra for both UQ and MQ₀. The band due to single mode vibrations are not shifted. In addition to that, the coupled vibrations are slightly deviated and deviation is less than 3 cm⁻¹. It further strengthens our conclusion that the addition of side group does not bring change in the nature of the spectra.

iii. The Solvent Effect

Table 3: Bond length of carbonyl group and C=C_r in (Å) unit of optimized structure of UQ, and MQ_O in Gas Phase (GP), CCl₄, and Crystal Structure (CS).

Types	C ₁ =O			C ₄ =O			C ₂ =C ₃			C ₅ =C ₆		
	GP	CCl ₄	CS	GP	CCl ₄	CS	GP	CCl ₄	CS	GP	CCl ₄	CS
MQ _O	1.223	1.225	1.234	1.231	1.232	1.232	1.364	1.364	1.404	1.354	1.354	1.419
UQ	1.223	1.225	1.234	1.231	1.232	1.232	1.364	1.364	1.404	1.354	1.355	1.419

By analyzing table (3) and figure (8), we came to the conclusion that frequency of both UQ and MQ_O decreased in the solvent phase calculation than that of in the gas phase in the 1800-1600 cm⁻¹ region. As a matter of fact, amount of decrement of particular IR band depend upon amount of change in bond length of the functional group that contributes to that specific band and they follows inverse relation. For example, bond length of C=C remains almost same for both types of quinones in both phase calculations. Hence, very slight decrement in the band at 1653 cm⁻¹, that is occurred predominantly due to antisymmetric C=C_r (C₂=C₃ and C₅=C₆) vibration coupled to the C₄=O vibration, is observed. On the other hand, C₁=O mode shifted down nearly by 11 cm⁻¹ and hence corresponding bond length increases by 0.002 Å. Similarly, lengthing of C₄=O (of UQ and MQ_O) by 0.001 Å leads to the lowering of bands at 1702 cm⁻¹ (UQ) and 1705 cm⁻¹ (MQ_O) to 1695 cm⁻¹ (UQ) and 1696 cm⁻¹ (MQ_O).

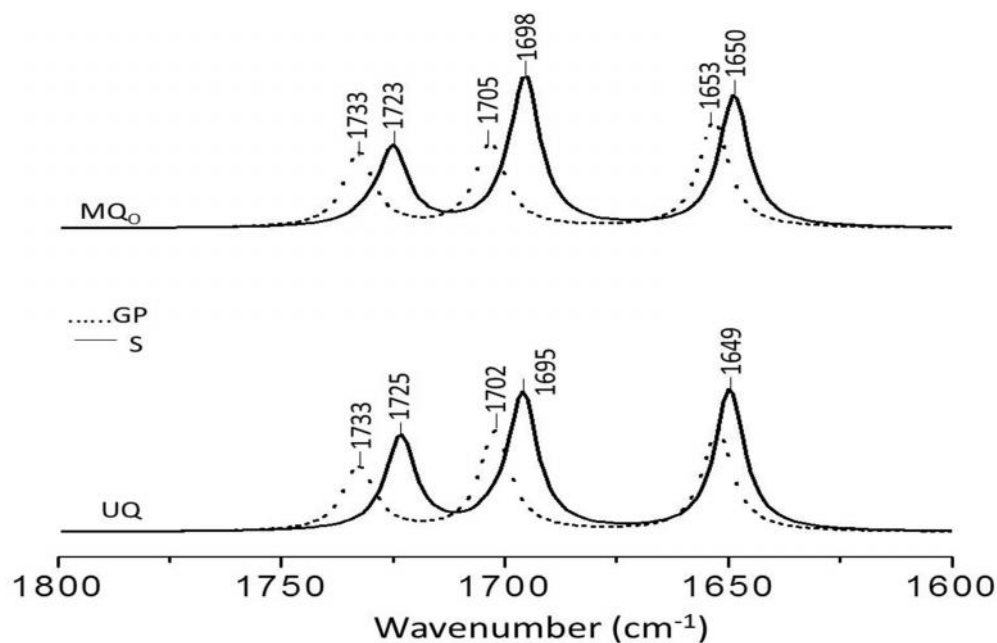


Fig. 8: Comparative spectra of UQ and MQ_O in gas phase and CCl₄. The Spectra are generated from the calculated stick spectra by convolving with Gaussian function of wavenumber 4 cm⁻¹.

4. Conclusions

By studying IR spectra in gas phase and CCl_4 of two different benzoquinones (with and without methoxy side group), we reach to the following conclusions. For the benzoquinones without methoxy side group (benzoquinone, duroquinone, and plastoquinone) two prominent IR bands are observed. The highly intense band is due to asymmetric C=O ($\text{C}_1=\text{O}$ and $\text{C}_4=\text{O}$) vibration, while weak one is due to asymmetric C=C_r ($\text{C}_2=\text{C}_3$ and $\text{C}_5=\text{C}_6$) vibration. But, for the benzoquinones with methoxy side groups (ubiquinone, dimethoxy dimethyl benzoquinone) three prominent IR bands in different (high/intermediate/low) frequency is observed. Here, high/intermediate/low frequency bands are due to C1=O/coupled C₄=O and C₂=C₃/ coupled asymmetric C=C_r and C₄=O vibration. Moreover, addition of methyl side groups lowered the band positions carbonyl vibrations in proportion to the number of methyl groups. Furthermore, upon solvent phase calculation prominent lowering in the intense carbonyl band is seen.

Acknowledgement

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