A First Principles Density-Functional Calculation of the Electronic and Vibrational Structure of the Key Melanin Monomers*

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We report first principles density functional calculations for hydroquinone (HQ), indolequinone (IQ) and semiquinone (SQ). These molecules are believed to be the basic building blocks of the eumelans, a class of bio-macromolecules with important biological functions (including photoprotection) and with potential for certain bioengineering applications. We have used the ∆SCF (difference of self consistent fields) method to study the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), ∆HL. We show that ∆HL is similar in IQ and SQ but approximately twice as large in HQ. This may have important implications for our understanding of the observed broad band optical absorption of the eumelans. The possibility of using this difference in ∆HL to molecularly engineer the electronic properties of eumelans is discussed. We calculate the infrared and Raman spectra of the three redox forms from first principles. Each of the molecules have significantly different infrared and Raman signatures, and so these spectra could be used in situ to non-destructively identify the monomeric content of macromolecules. It is hoped that this may be a helpful analytical tool in determining the structure of eumelanin macromolecules and hence in helping to determine the structure-property-function relationships that control the behaviour of the eumelans.

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I. INTRODUCTION

The melanins are an important class of pigmentary macromolecule found throughout the biosphere 1. Pheomelanin (a cysteinyldopa derivative) and eumelanin (formed from 5,6-dihydroxyindolequinone and other indolequinones) are the predominant forms in humans, and act as the primary photoprotectant in our skin and eyes. Consistent with this role, all melanins show broad band monotonic absorption in the UV and visible in the range 1.5 to 5 eV 2. In contrast, other biomolecules such as proteins and nucleic acids show only well defined absorption peaks around 280 nm (4.5 eV) and little absorption below that 3. They are also efficient free radical scavengers and antioxidants 4. In direct contradiction with these photoprotective properties, both pheomelanin and eumelanin are implicated in the development of melanoma skin cancer 4. For this reason, the photophysics, photochemistry and photobiology of melanins are subjects of intense scientific interest.

Despite work over several decades (with respect to eumelanin in particular), the more general structure-property-function relationships that control the behaviour of these important bio-macromolecules are still poorly understood 2. The melanins are difficult molecules to study: they are chemically and photochemically stable, and are virtually insoluble in most common solvents. It is fairly well accepted that eumelans are macromolecules of the various redox forms of 5,6-dihydroxyindolequinone (DHI or HQ) and 5,6-dihydroxyindole 2-carboxylic acid (DHICA) 1,2. However, major questions still remain concerning their basic structural unit 2. Two opposing schools of thought exist: i) that eumelans are composed of highly cross-linked extended hetero-polymers consistent with the Raper-Mason scheme 1, and ii) that eumelans are actually composed of much smaller oligomers condensed into 4 or 5 oligomer nano-aggregates 3. Clearly, this is a fundamental issue, and is the starting point for the construction of consistent structure-property-function relationships.

The answer to this question also has profound implications for our understanding of the condensed phase properties of melanins. In 1960 Longuet-Higgins 4, in a landmark paper, proposed that many of the physical properties of melanins could be understood if they were semiconductors. This proposition was lent further support by Pullman and Pullman 14 in 1964 who applied molecular orbital theory in its simplest form (the Hückel approximation) to 5,6-dihydroxyindole and one particular dimer type. This theoretical work was followed in 1974 by the experimental observations of McGinness, Corry and Proctor who demonstrated that a pellet of melanin could be made to behave as an amorphous electrical switch 11. They postulated that these materials may indeed be disordered organic semiconductors consistent with the Longuet-Higgins theory, and the newly developed models of amorphous inorganic semiconductors 12. Several
studies since have also claimed to show that melamins in the condensed solid-state are semiconductors. However, it is by no means certain that the conductivity reported in any of these experimental studies is electronic in nature. A clear idea of the basic structural unit is crit
cal to developing a consistent model for condensed phase charge transport in such disordered organic systems. It is also important in the context of “molecularly engineering” melamins to have the ability to create or enhance functionality in high technology applications such as biosensors and bio-mimetic photovoltaics.

It is well known that disorder plays a crucial role in de
termining the charge transport properties of amorphous inorganic semiconductors. In addition to the usual impurity related disorder, organic semiconductors (of which eumelanin may well be an exotic example), present several different sources of disorder associated with structural heterogeneity. For example, if one considers either the hetero-polymer or oligomer models, there are many different ways of constructing a eumelanin macro-
molecule based upon the monomer sequences, cross-linking positions or tautomer combinations. These pos-
sibilities have been studied theoretically for DHI-based macromolecules using a number of quantum chemical techniques. Notably, Galvao and Caldas used the Hückel approximation to construct model homo-
polymers. Intriguingly, they found that many of the im-
portant “semiconductor related properties of eumelanin” stabilise at a relatively small number of monomer units - five or six in fact. Although they did not consider inter-chain effects, and essentially treated chain termina-
tions as end defects, their work was the first indication that large, extended hetero-polymeric structures are not required to explain the physical properties of melamins. Bolivar-Marinez et al. and Bochenek and Gudowska-
Nowak have used the intermediate neglect of differ-
ential overlap (INDO) and other semi-empirical methods to perform similar calculations for oligomers, whilst other authors have utilised the power of density functional the-
orical approximation to perform first principles calculations on single monomers or dimers.

Il’ichev and Simon considered the hydroquinone, (HQ) and indolequinone (IQ) forms (see figure), and determined them to be the most stable and hence the most likely forms of the monomers. However, several pulse ra-
diolysis studies have indicated the presence of the semiquinone (SQ - also shown in figure), a tautomer of IQ, and so we also consider SQ here.

Motivated by the remarkable optical absorption char-
acteristics of eumelans, many of these authors have fo-
cused on simulating the absorption spectra of HQ, IQ, SQ and related small oligomers. However, knowledge of the electronic states around the highest occupied molecular orbital (HOMO) and lowest unoc-
cupied molecular orbital (LUMO) levels is only part of the story. A great deal of information is also contained within the vibrational and rotational structure of the molecules. In particular, the IR and Raman spectra may be useful analytical tools. This has proven to be the case in other biomolecules. They can be used to con-
firm the accuracy of the first principles predictions by direct comparison with experimental evidence, and also to provide useful insight into local environment phenomena such as solvent-solute interactions. Furthermore, our IR and Raman spectra calculations have the advantage of coming from first principles calculations and not the semi-empirical methods often employed to calculate the absorption spectra.

In this paper we present a full density functional theory (DFT) analysis of the electronic, vibrational and rotational structure of the indolequinone (IQ), the semiquinone (SQ) and the hydroquinone (HQ). Our study is a considerable extension of previously published work since we: i) present calculated IR and Raman spec-
tra for the first time, and ii) use the difference of self con-
sistent fields (ΔSCF) approach to gain a more accurate understanding of the LUMO level. We find that the electronic properties of the molecules are highly dependent upon the redox form. Hence, we can say that oligomers or hetero-polymers consisting of one or more redox forms will have large variations in the local chemical potential, or, in the language of the tight binding model, strongly random site energies and possibly also random hopping integrals. This is to say that such hetero-structures will be highly disordered.

Our work is motivated by the desire to understand the implications of the redox form of the basic structural unit of eumelans on the materials bulk properties. Such knowledge is a key starting point in any attempts to under-
stand charge transport in and the optical properties of these disordered heterogeneous organic conductors. It also has profound implications in unravelling the mysteries of melanin biological functionality, and attempts to molecularly engineer melanin-like molecules for technolo-
gical applications. These preliminary theoretical cal-
culations are part of an ongoing quantum chemical, ex-
perimental solid-state and spectroscopic program aimed at gaining a more complete understanding of melanin structure-property-function relationships.

II. CALCULATION DETAILS

The chemical and electronic structures and the Raman and IR spectra were found from first principles DFT cal-
culations. We have performed our calculations using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) and NRLMOL performs massively parallel electronic structure calculation using gaussian orbital methods. In particular, for a discussion of the calculation of the Raman and IR spectra see Refs. Throughout we have used the Perdew, Burke and Ernzerhof (PBE) exchange correlation functional, which is a generalised gradient approx-
imation (GGA) containing no parameters. For each molecule we have fully relaxed the geometry with no sym-
FIG. 1: Schematic representation of the 5,6-dihydroxyindolequinone (DHI) redox forms: hydroquinone (HQ) and the tautomers indolequinone (IQ) and semiquinone (SQ). The numbers correspond to those used in table II.

TABLE I: The total energy (in eV) of the two lowest energy tautomers of indolequinone (IQ); semiquinone (SQ) and 2-semiquinone (2-SQ) which is simply SQ with the hydrogen atom bonded to O11 rather than O10 (c.f. figure 1). The energies are quoted relative to the energy of IQ. In each case we fully relaxed the geometries as shown in figures 3 and 4. Our results for HQ, IQ and SQ are consistent with the calculations of Il’ichev and Simon [22]. The concentrations at 300 K are in direct contradiction to the experimental evidence [23, 24, 25, 26, 27, 28] that SQ is one of the building blocks of eumelanin.

| Molecule | Name in Ref. 22 | Energy (eV) | Concentration at T = 300 K |
|----------|----------------|-------------|----------------------------|
| IQ       | 3a             | 0           | 87%                        |
| 2-SQ     | 3d             | 0.05        | 13%                        |
| SQ       | 3c             | 0.19        | < 0.1%                     |

III. RESULTS AND DISCUSSION

To benchmark our calculations we report the bond lengths and bond angles of HQ, IQ and SQ found in our calculations in table II. Our results are in good agreement with those calculated by Bolivar-Marinez et al. [20] and Stark et al. [5]. All three molecules are planar to within numerical accuracy (c.f., 2, 22).

We find, in agreement with Il’ichev and Simon [22], that SQ is not the lowest energy tautomer of IQ (see figure 1). Indeed we find that at 300 K there should be less than 0.1% SQ. Although we should stress that this calculation is for a single molecule in vacuo it is, of course, in direct contradiction to the evidence [23, 24, 25, 26, 27, 28] that SQ is one of the building blocks of eumelanin. However, since SQ is widely thought to play an important role in eumelanin, we also consider it here.

As well as the ground state geometries shown in figures 2, 3 and 4 we also found stable geometries of HQ and SQ with the H-O-C bond angle increased by almost 180°. These alternative structures have significantly higher energies than the ground states. However, it is possible that the high energy structures may be stabilised by hydrogen bonding in a polar solvent. We therefore also considered the system SQ + 6H₂O. We found that in this system the H-O-C bond is slightly larger than in SQ in vacuo (see figure 5). We also found a significant hydrogen bonded network around the H-O-C-C=O group which is dragged out of the plane of the molecule by interactions with the water molecules. This hydrogen bonding network is probably related to the fact that eumelanins are only soluble in polar solvents.

The Hückel model calculations of Galvao and Caldas [17] indicate that the HOMO-LUMO gap (Δ_HL) may be significantly larger in HQ than in either IQ or SQ. This has important implications in the context of understanding the basic eumelanin structural unit. Fundamentally, a combination of HQ and either IQ or SQ tautomers are present in an ensemble. Whether that ensemble be oligomeric or polymeric it can be expected to lead to an
apparent broadening of the absorption profile. In this situation, the key question is: how many monomers of HQ, IQ and SQ are required to create the broad band UV and visible absorbance over the range 1.5 to 5 eV that is macroscopically observable for eumelanins? The answer to this question may well allow us to assess the feasibility of the various structural models. Furthermore, when one considers the possibility that molecularly engineered forms of eumelanin may be useful as functional materials in electronic devices and sensors \cite{13, 16}, a critical design parameter is likely to be the “semiconductor” gap. It has previously been shown \cite{18} that, at least within the Hückel approximation for homopolymers, the HOMO-LUMO gap of the monomer is closely related to the HOMO-LUMO gap of the infinite polymer, which, for the polymer model in the condensed solid state, corresponds to the semiconducting gap provided there is only weak coupling between polymers. Thus controlling the HOMO-LUMO gap of macromolecules may provide a route to controlling the semiconducting gap of eumelanins. This suggestion clearly needs further investigation, but controlling the HQ to IQ or SQ ratio may be a possible route to this form of property manipulation. An important first step to investigating either of these proposals is the calculation of the HOMO-LUMO gaps of the molecules by more reliable methods than Hückel theory.

In table \text{III} we compare the HOMO-LUMO gap found in our calculations with that found from the Hückel method \cite{17}. For comparison with the Hückel calculations we need to estimate the hopping integral, \( \beta \), in the Hückel Hamiltonian,

\[
\hat{H} = \sum_{i} \left( \epsilon_{i} + \alpha \delta_{i} \right) \hat{c}_{i \sigma} \hat{c}_{i \sigma}^{\dagger} - \beta \sum_{i} \sum_{j} \delta_{i \sigma} \hat{c}_{i \sigma}^{\dagger} \hat{c}_{j \sigma}, \tag{1}
\]

where \( \alpha \) is the on-site energy, \( \alpha' \) is the difference in the on-site energy between a nitrogen and a carbon atom (we take the labelling convention from figure \textbf{1}, ensuring that the only nitrogen is in position \( i = 9 \)), \( \epsilon_{i} \), \( \hat{c}_{i \sigma} \) annihilates (creates) an electron with spin \( \sigma \) on site \( i \) and \( \langle ij \rangle \) indicates that the sum is over nearest neighbours only. For hydrocarbons \( \beta \) is typically of order 2.5 eV \cite{37}. Using this value of \( \beta \) we find that the HOMO-LUMO gaps for HQ, IQ and SQ found from the Hückel approximation are consistent with those found in our DFT calculations using the PBE functional. However, because DFT is a theory of the ground state, these calculations represent the energy gap between Kohn–Sham eigenvalues and not the true HOMO-LUMO gap of the molecules. This is known as the band gap problem \cite{38}. Additionally, it is accepted that the PBE functional can significantly underestimate the HOMO-LUMO gap. Therefore we have also employed the \text{∆SCF} method \cite{38} to calculate \( \Delta_{HL} \). Our results clearly reproduce the trends seen in the time dependent density functional theory (TDDFT) calculations of Il’ichev and Simon \cite{22} for IQ and SQ. The difference between the \text{∆SCF} and TDDFT results for HQ probably indicates that the true value of \( \Delta_{HL} \) is intermediate to the values predicted by the two different methods as it is extremely unlikely that either method is incorrect by a large enough margin to allow the other to be correct.

The calculated \text{∆SCF} HOMO-LUMO gap is also consistent with previously published semiempirical ZINDO (Zerner’s intermediate neglect of differential overlap) calculations of the optical absorption spectra \cite{12, 20}. In particular Bolivar-Marinez et al. noted that “in the neutral state the threshold for optical absorption is around 2.0 eV for the IQ and SQ, while in the case of the HQ it is roughly 3.8 eV.” Taking these numbers as semiempirical estimates of the HOMO-LUMO gap they are in excellent agreement with our \text{∆SCF} calculations (c.f. table \text{III}).

It is also interesting to note that the change in the SQ conformation observed in the calculations for the SQ + 6H2O system caused a 7% decrease in \( \Delta_{HL} \) relative to SQ in vacuo. It is possible that in a polar solvent a range of conformations exist which may lead to a broadening of the optical absorption \cite{39}.

In terms of Hückel theory, the difference between \( \Delta_{HL} \) for HQ and IQ/SQ can be understood in terms of the level of delocalisation of the HOMOs and LUMOs. It should be noted that the aromatic ring in HQ contains

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & IQ & SQ & HQ \\
\hline
TDDFT (PBE/B3LYP) \cite{22} & 1.82 & 1.50 & 4.53 \\
TDDFT (B3LYP) \cite{22} & 1.79 & 1.43 & 4.30 \\
NRLMOL (\text{∆SCF}/PBE) & 2.02 & 1.12 & 3.61 \\
NRLMOL (PBE) & 1.07 & 0.80 & 3.48 \\
Hückel \cite{17} & 1.3 & 0.84 & 3.4 \\
\hline
\end{tabular}
\caption{The HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gap, \( \Delta_{HL} \), in eV.}
\end{table}
FIG. 2: The electron density in the highest occupied molecular orbital (HOMO) (top) and the lowest unoccupied molecular orbital LUMO (bottom) of hydroquinone (HQ). The atoms are colour coded as follows: carbon - green, nitrogen - blue, oxygen - red and hydrogen - white. The LUMO electron density is in good agreement with the semiempirical calculations of Boliar-Marinez et al. [20], however there is some discrepancy in the HOMO electron density.

In the absence of knowledge of the chemical structure of the eumelanins it is difficult to predict how a change in the HOMO-LUMO gap of the monomer will effect the electronic structure. However it is likely that changing $\Delta_{HL}$ by a factor of two will have a dramatic effect on the electronic structure of the melanin macromolecule. For example, it is reasonable to expect that the HOMO-LUMO gap of a macromolecule will be related to $\Delta_{HL}$ (c.f. Ref. [18]). Thus we expect that the HOMO-LUMO gap for a macromolecule of HQ will be significantly larger than that of a macromolecule of IQ or SQ. For a macromolecule of HQ the HOMO-LUMO gap is a factor of two larger than that of SQ and IQ. However, even in the $\Delta$SCF calculation, the HOMO-LUMO gap is a factor of two larger in HQ than it is in SQ and IQ.
TABLE IV: The predicted Phonon (IR) and Raman spectra for hydroquinone (HQ).

| Frequency (cm$^{-1}$) | IR intensity (D$^2$/amuÅ$^2$) | Isotropic Raman scattering activity (Å$^4$/amu) | Total Raman scattering activity (Å$^4$/amu) |
|----------------------|-------------------------------|-----------------------------------------------|-------------------------------------------|
| 137.4                | 0.008                         | 0.000                                         | 0.668                                     |
| 144.0                | 0.162                         | 0.000                                         | 0.605                                     |
| 289.5                | 0.357                         | 0.000                                         | 0.729                                     |
| 300.7                | 0.389                         | 0.022                                         | 0.908                                     |
| 302.9                | 1.848                         | 0.000                                         | 2.430                                     |
| 311.7                | 0.976                         | 0.000                                         | 1.205                                     |
| 314.0                | 0.019                         | 0.023                                         | 0.533                                     |
| 344.3                | 0.932                         | 0.000                                         | 0.040                                     |
| 366.5                | 1.360                         | 0.000                                         | 0.993                                     |
| 416.0                | 0.145                         | 0.000                                         | 0.990                                     |
| 428.2                | 0.120                         | 0.013                                         | 3.523                                     |
| 463.2                | 0.032                         | 9.290                                         | 14.050                                    |
| 589.6                | 0.040                         | 0.000                                         | 0.380                                     |
| 608.8                | 0.561                         | 0.000                                         | 1.277                                     |
| 665.2                | 0.581                         | 0.000                                         | 0.520                                     |
| 677.4                | 0.376                         | 0.000                                         | 0.626                                     |
| 706.8                | 0.689                         | 0.000                                         | 0.811                                     |
| 735.0                | 0.011                         | 31.978                                        | 36.825                                    |
| 753.5                | 0.036                         | 0.178                                         | 1.655                                     |
| 762.5                | 0.506                         | 0.000                                         | 0.947                                     |
| 806.4                | 0.436                         | 0.000                                         | 0.776                                     |
| 843.0                | 0.639                         | 0.477                                         | 0.636                                     |
| 890.6                | 0.125                         | 2.517                                         | 4.183                                     |
| 1055.2               | 0.291                         | 21.980                                        | 28.451                                    |
| 1069.8               | 0.129                         | 0.213                                         | 2.528                                     |
| 1104.2               | 2.271                         | 1.698                                         | 2.285                                     |
| 1145.8               | 0.635                         | 0.034                                         | 9.197                                     |
| 1159.9               | 8.026                         | 0.708                                         | 1.406                                     |
| 1175.8               | 2.970                         | 0.000                                         | 3.764                                     |
| 1217.1               | 0.303                         | 1.202                                         | 2.299                                     |
| 1265.2               | 0.391                         | 5.638                                         | 8.478                                     |
| 1328.6               | 0.909                         | 26.707                                        | 45.852                                    |
| 1334.9               | 1.440                         | 3.164                                         | 4.150                                     |
| 1360.6               | 0.213                         | 68.155                                        | 122.963                                   |
| 1425.4               | 0.135                         | 1.951                                         | 12.385                                    |
| 1462.3               | 2.384                         | 3.954                                         | 38.040                                    |
| 1489.8               | 0.324                         | 0.016                                         | 0.614                                     |
| 1511.3               | 1.122                         | 64.105                                        | 92.156                                    |
| 1503.6               | 0.436                         | 0.005                                         | 1.408                                     |
| 1628.4               | 0.366                         | 3.559                                         | 21.170                                    |
| 3086.8               | 0.425                         | 30.403                                        | 58.297                                    |
| 3090.6               | 0.257                         | 90.643                                        | 170.535                                   |
| 3170.7               | 0.047                         | 2.066                                         | 86.139                                    |
| 3189.4               | 0.033                         | 128.345                                       | 185.587                                   |
| 3598.1               | 1.359                         | 78.683                                        | 135.123                                   |
| 3709.9               | 1.153                         | 74.758                                        | 126.550                                   |
| 3716.9               | 1.182                         | 98.150                                        | 155.123                                   |

FIG. 5: The stable structure of semiquinone (SQ) and 6 H$_2$O molecules. Note the hydrogen bonded networks around the H-O-C-C=O group, which is dragged slightly out of the plan by the interactions with the solvent. The H-O-C bond angle has increased relative to that of the SQ molecule in vacuo.

It is also difficult, without detailed knowledge of the chemical structure of the eumelans, to predict exactly how the variation of $\Delta_{HL}$ affects the optical absorption. However, it seems possible that the range of $\Delta_{HL}$ between different molecules may produce the continuum of HOMO-LUMO gaps in eumelanin macromolecules and thus play an important role in explaining the observed the broad band optical absorption.

It is therefore important to be able to identify the monomeric content of a sample of eumelanin, ideally this should be done in situ and non-destructively. Motivated by this fact we have calculated both the Raman and infrared (IR) spectra of IQ, SQ and HQ, (see tables IV, V and VI). This has several uses. Firstly, the prediction allows for experimental testing of the accuracy of our calculations. Secondly, it can be seen that there are notable differences in both the Raman and IR spectra of the three monomers (see, for example, figures 6 and 7). The Raman and IR spectra could therefore be used for the in situ, non-destructive identification of the monomeric content of macromolecules. This could be particularly valuable in the engineering of devices from eumelans, as, by varying the ratio of indole-quinones, it may be possible to achieve control of the band-gap of the material. This may also be a useful analytical tool for the analysis of the structure of both synthetic and naturally occurring melanin, and thus be helpful in determining the structure-property-function relationships that control their behaviour.

Comparison of our calculated IR and Raman spectra with standard tables for organic molecules [40, 41] shows that the calculated phonon spectra are in broad agreement with known IR absorption band values (see table VII). It can also be seen from table VII that the differences in the spectra, specifically which vibrations are absent for a given molecule can be understood in terms of

molecule containing both HQ and, say, IQ this change in the electronic structure will act as a source of disorder and thus have a dramatic effect on the electronic transport properties.

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of their structure, c.f. figure 1 as expected.

It is important to stress that our calculated IR and Raman spectra are for gaseous phase monomers. Thus, the comparison of such results with experiment may be complicated by several factors. Firstly the formation of macromolecules may result in a significant change in the spectra. However, it is known that in other biomolecules the effect of polymerisation only slightly broadens the IR and Raman spectra, for example the spectra of simple amino acids is only slightly broadened in proteins 42. Secondly solvent effects may largely ‘wash out’ the individual features of the spectra 33, 43. It is clear from our study of the SQ + 6H2O system that there will be significant hydrogen bonding in the solvent, hydrogen bonding can shift the phonon frequencies 3. Therefore it remains to be seen if, experimentally, the resolution is good enough to resolve the differences in the spectra of the monomers. However, an obvious way to avoid solvent effects is to conduct the experiments in the solid state.
TABLE VII: Broad assignments of the strongest bands in the simulated phonon (IR) spectra of HQ, SQ and IQ (FIG.6). The band assignments were made according to standard tables [40, 41].

| Band (cm\(^{-1}\)) | Group/Vibration | HQ     | SQ     | IQ      |
|---------------------|----------------|--------|--------|---------|
| ~1100               | \(\nu\) (C-OH) strong | present| present| absent  |
| ~1340               | \(\nu\) (Aromatic C-N) strong | present| absent| present |
| ~1450-1590          | \(\nu\) (Aromatic C-C) strong | present| present| present |
| ~1620-1650          | \(\nu\) (quinone C=O) strong | absent| present| present |
| ~3590-3600          | \(\nu\) (N-H) medium | present| absent| present |
| ~3700               | \(\nu\) (O-H) strong | present| present| absent  |

IV. CONCLUSIONS

We have carried out first principles density functional calculations for the hydroquinone (HQ), the indolequinone (IQ) and the semiquinone (SQ). The calculated gaseous phase structure is in good agreement with previous calculations. We have used the \(\Delta\)SCF method to study the HOMO-LUMO gap. Our results are consistent with the threshold for optical absorption found by semiempirical methods. Specifically, we found that the HOMO-LUMO gap is similar in IQ and SQ but approximately twice as large in HQ. The possibility of using this difference in the HOMO-LUMO gap to engineer the electronic properties of eumelanins at the molecular level has been discussed. We have also suggested that the difference in the HOMO-LUMO gap of the different monomers could lead to a large range of HOMO-LUMO gaps in eumelanin macromolecules and thus be related to the observed broad band optical absorption.

As the structure of macromolecules of these monomers is not known we have also calculated the IR and Raman spectra of the three monomers from first principles. A comparison of these results with experiment would represent a stringent test of the density functional calculations as these calculations do not rely on additional semiempirical information. It was shown that the IR and Raman spectra have potential as a analytical tool for these materials. Each of the monomers have significantly different spectral signatures, therefore the IR or Raman spectra could be used in situ to non-destructively investigate the monomeric content of macromolecules. It is hoped that this may be helpful in determining the structure of both natural and synthetic eumelanins, and hence aid our attempts to understand their biological functionality.

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FIG. 6: Detail of the phonon (IR) spectra of hydroquinone (HQ) (solid line), semiquinone (SQ) (dashed line) and indolequinone (IQ) (dotted line). Clear differences can be seen between the spectra of the three monomers. For example, there are strong features around 1100 cm$^{-1}$ in both HQ and SQ but not in IQ. On the other hand, there are strong bands between $\sim$1620 and 1650 cm$^{-1}$ in SQ and IQ which are absent in HQ (for broad assignments see Table VII). This confirms that the IR spectra could be useful as in situ, non-destructive probes for identifying the monomeric content of eumelanins. To allow us to plot the spectra and to aid comparison with experiment we have broadened each peak by 6 cm$^{-1}$, a value that is comparable to that seen experimentally for other biomolecules in solution.

FIG. 7: Detail of the Raman spectra of hydroquinone (HQ) (solid line), semiquinone (SQ) (dashed line) and indolequinone (IQ) (dotted line). Once again, there are clear differences between the spectra of the three monomers confirming that Raman spectra could be useful as in situ, non-destructive probes for identifying the monomeric content of eumelanins. To allow us to plot the spectra and to aid comparison with experiment we have broadened each peak by 6 cm$^{-1}$, a value that is comparable to that seen experimentally for other biomolecules in solution.