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IR spectral fingerprints of carbonyl groups in graphite oxide: a theoretical study

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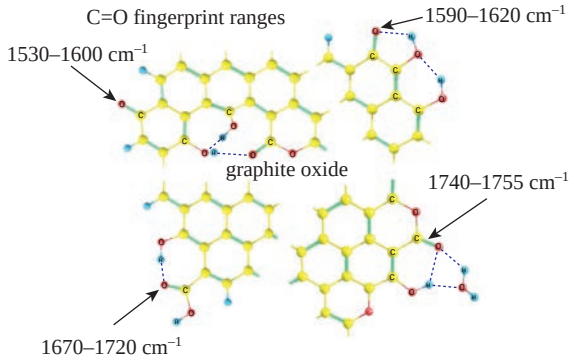
Non-empirical quantum chemical calculations of various possible fragments in the oxidized carbon layer of graphite oxide were carried out at the DFT level with the hybrid B3LYP functional and the extended double-zeta Gaussian basis set. These fragments contain the carbonyl groups as ketone, carboxyl and lactone functions, either free or hydrogen-bonded to hydrating water molecules or closely arranged hydroxyl groups. Using the vibrational energy distribution analysis, the typical spectral ranges of C=O vibrations were identified within the fingerprint region of 1550–1800 cm^{-1} depending on the kind of the carbonyl group studied and its environment.



Keywords: graphite oxide, quantum chemical calculations, carbonyl vibrations, typical frequency ranges, ketone group, carboxyl group, lactone group.

Graphite oxide (GO), discovered more than a century and a half ago,[1] attracts increased attention of researchers due to its almost unique structure, whose modification in various ways allows one to obtain materials that can be used in catalysis, drug delivery, as hydrogels, *etc*. The result of chemical modification, of course, depends on the composition of the starting material and the chosen method. In the case of GO, which has an irregular multilayer structure, the question of structural changes remains a key one. The average composition of GO layers depends on the oxidation degree, determined by the combination of oxidants and the duration of the process, and on the degree of dehydration during repeated washing procedures following the formation stage.[2–7] The C/O ratio, which is one of the GO signatures, ranges from 1.17 and 1.15 in early syntheses[2,3] to 0.84 and 0.74 in relatively recent ones.[4,6] Thus, modern techniques provide a higher degree of oxidation, which means that the total area of non-oxidized segments of the graphite layer is smaller, but the relative number of different oxygen-containing functional groups remains unknown. To a certain extent, it is solved by analyzing IR absorption and NMR spectra, the assignment of signals in which is based on the known characteristic ranges of various expected groups. However, the effect of an extended carbon skeleton should never be ignored, especially when its conjugated segments are adjacent to the groups of interest. These segments should play an especially pronounced role when the functional group itself includes a double bond that provides its coupling to an adjacent conjugated structure segment. The carbonyl group is a group of this very kind and represents a methodically good example of a probing functional group in the structure of GO.

It is impossible to shed light on the coupling mentioned above and to determine the characteristic absorption ranges only based on experimental data. Here, quantum chemical calculations are of indispensable value. There are published data of this kind.[8–11] For example, the following frequencies were found[8] for the C=O group within various structural elements: 1715–1718, 1740 and 1812 cm^{-1} in the ketone, carboxyl and lactone groups, respectively. In other investigations,[9,10] the vibrations of the C=O group were found to fall within the broader general ranges of 1744–1826 or 1750–1850 cm^{-1}, decreasing in a series[9] of the following parent groups: 5-membered lactone (~1830 cm^{-1}) > anhydride (1740–1810 cm^{-1}) ≈ 6-membered lactone (1790 cm^{-1}) > carboxyl group (~1750 cm^{-1}). The role of the environment was also studied, and it was found[9] that a hydroxyl group located close causes a redshift of *ca*. 90 cm^{-1} for the C=O vibrations in 5- and 6-membered lactones and carboxyl groups. The vibrations in the range of 1600–1750 cm^{-1} were assigned[10,11] to carboxyl groups and water molecules, with water[11] around 1650 cm^{-1} and carbonyl groups[11] around 1735 cm^{-1} playing the predominant role. Thus, though most of the spectral signatures of C=O groups seem to be clarified, the function of hydrating water molecules and their joint action with specific combinations of neighbouring oxygen-containing functional groups remain unclear. This issue is of high importance because it is impossible to remove water from GO samples completely during even a long evacuation.

In this study, model systems were constructed based on a C_{54} segment of the graphene sheet decorated with functional groups. Ketone groups were added on either the outer edge of the sheet or the edge of a small internal defect. Given the high probability of the presence of hydroxyl groups near carbonyl groups, they were added in various amounts together with water molecules. Models of the following general composition were considered: $C_nH_m(O)_k(OO)_l(OOH)_p(OH)_q(COOH)_r(H_2O)_s$, where C_nH_m denotes the carbon skeleton terminated, if necessary, with hydrogen atoms, while (O), (OO), (OOH), (OH) and (COOH) denote ketone, lactone, lactol, hydroxyl and carboxyl groups, respectively ($30 \leqslant n \leqslant 58$, $10 \leqslant m \leqslant 18$, $0 \leqslant k \leqslant 2$, $0 \leqslant l \leqslant 4$, $0 \leqslant p \leqslant 2$,

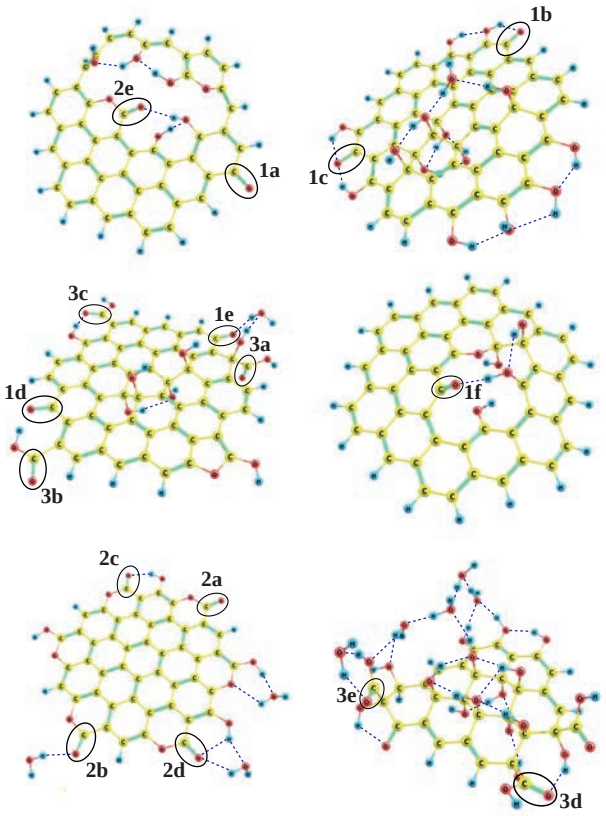


Figure 1 The minimum-energy structures of GO model systems with the composition $C_nH_m(O)_k(OO)_l(OOH)_p(OH)_q(COOH)_r(H_2O)_s$ considered in this work.

$2 \leqslant q \leqslant 6$, $0 \leqslant r \leqslant 3$ and $0 \leqslant s \leqslant 3$). The model systems were constructed in such a way that they can represent various fragments of GO, where at a given average degree of oxidation, the more oxidized segments can be adjacent to the non-oxidized parts of the graphite layer, as well as to the parts where remote functional groups can be found, judging by ultra-high-resolution transmission electron microscopy images.[12]

The structures were optimized at the density functional level using the hybrid B3LYP functional and a combined basis set consisting of 6-31G sets on the carbon atoms of the skeleton and 6-31G(d,p) sets on all the atoms of functional groups (Figure 1). To scale the frequencies of normal vibrations, the following average coefficients were taken from the available literature data[13–18] for cyclohexanone, acetone, *p*-benzoquinone, β-propiolactone, coumarin, benzoic and acetic acids and their dimers in the range of 1550–1800 cm^{-1}, namely, 0.970, 0.961 and 0.984 for ketone, carboxyl and lactone groups, respectively. The simulation was performed using the Firefly 8.2 software package[19] and the results were visualized using the Chemcraft software.[20] Normal vibrations were considered based on internal coordinate shifts and assigned to particular functional groups when the main contribution to the vibrational energy distribution (VED) was made by one or several groups of the same kind. The corresponding analysis was carried out using the VEDA software.[21]

The ketone group located on the outer edge of the carbon sheet can stand alone (Figure 1, group **1a**) or be surrounded by hydroxyl groups on both sides (Figure 1, group **1c**). It also can be adjacent to a hydroxyl group (Figure 1, group **1b**), a carboxyl group (Figure 1, group **1d**) and a combination of hydroxyl and carboxyl groups (Figure 1, group **1e**). The latter combination was extended with a water molecule to clarify the relative proton-donor and proton-acceptor capabilities of the various groups. Within a small defect, the ketone group can be opposite to the hydroxyl or carboxyl group (Figure 1, group **1f**), which adds some new features, taking into account the relative position of the groups.

When the ketone group is the only local modifier of the graphite sheet edge (Figure 1, group **1a**) and the neighbouring part of the sheet is not oxidized, there is a strong coupling between the stretching vibrations of the C=O and C=C groups, and the contribution of the C=O group does not exceed 25%. The coupling is manifested in the broadening and redshift of the corresponding spectral range from 1660–1670 cm^{-1}, typical of diaryl ketones, to 1530–1635 cm^{-1}. The lower the frequency, the higher the contribution of those internal coordinates that correspond to the total distortion of the extended conjugated segment of the carbon sheet, *e.g.*, 86, 66 and 64% at 1527, 1585 and 1630 cm^{-1}, respectively. In the presence of a hydroxyl group attached to a neighbouring C atom (Figure 1, group **1b**), a relatively long hydrogen bond is formed between them, which causes an increase in the C=O distance by only 0.007 Å, so that a closed coordination pentagon appears. Nevertheless, the role of the hydroxyl group is not negligible, since its contribution to the VED of vibration with the frequency of 1614 cm^{-1} is about 13%, mainly due to the τ-vibration in the OH···O fragment. In addition, the frequency range of C=O vibrations is narrower (about 20 cm^{-1}), but still centered around 1600 cm^{-1} (1592–1614 cm^{-1}) and is characterized again by a comparable contribution from the effective internal coordinates describing distortions of relatively distant segments of the carbon sheet. The vibration with the frequency of ~1595 cm^{-1} can be considered as typical of such ketone–hydroxyl combinations due to the high contribution of C=O to VED (about 40%).

When the ketone group and the opposite hydroxyl group form a hydrogen bond in the internal defect (Figure 1, group **1f**), the conjugation of C=O and double C=C bonds in the carbon skeleton competes with partial conjugation of C=O and the hydrogen bond, which is also characterized by π-kind binding.[22] Also, the lactol group present in this defect further disrupts the conjugation with the adjacent segment of the carbon sheet. As a result, the (C–C)C=O fragment is tilted almost 45° to the average carbon plane, the coupling of the C=O and C=C stretching vibrations is weaker and the contribution of the C=O group to the VED is about 56%. When two hydroxyl groups are located on either side of the ketone group (Figure 1, group **1c**), and the adjacent part of the carbon skeleton retains a conditionally sp^2 character, a very rigid structural element consisting of several cycles appears. The C=O group itself is part of the C6 cycle and forms two H-bonded cycles. This coordination motif makes the ketone group almost stationary. In the frequency ranges indicated above, consistent distortions of only the hydroxyl groups are observed. It should be noted that, judging by the length of the hydrogen bond in the coordination hexagon (Figure 1, group **1c**) and the elongation of the C=O bond by 0.032 Å, this H-bond is relatively strong. Therefore, this closed structural element can be considered as very stable.

Thus, the lower the oxidation depth of graphite and, accordingly, the higher the fractional area of sp^2 carbon segments, the stronger the coupling between the stretching vibrations of possibly formed ketone groups and the distortions of the carbon skeleton, covering the spectral range from 1490 to 1590 cm^{-1}. Near the lower limit of the range, *i.e.*, around 1530 cm^{-1}, it is the distortion of the carbon skeleton that prevails, but even a small contribution from C=O provides a noticeable change in the dipole moment, which should lead to an increase in the observed absorption. The deeper the oxidation and, accordingly, the smaller the conjugated carbon segments and the greater the content of hydroxyl groups in the immediate vicinity of ketone groups, the higher the frequency of C=O vibrations, the vibrations characteristic of the C=O groups H-bonded to hydroxyl groups being in the range of 1590–1620 cm^{-1}.

A carbonyl group, if adjacent to the oxygen atom that replaces a carbon atom in the skeleton, acts as part of the lactone group. The replacement disrupts the conjugation within the carbon sheet on at least one side of the C=O group, which must inevitably affect the degree of coupling of internal coordinate distortions. As a result, the vibrations of carbonyl groups in lactones are more localized compared to those of ketone groups. Furthermore, the additional oxygen atom changes the proton-acceptor capability of the carbonyl group. For this reason, the following structural elements were considered: a separate lactone on the outer edge of the carbon sheet (Figure 1, group **2a**), a lactone group that can form a coordination bond with a hydrating water molecule (Figure 1, group **2b**), a lactone close to the hydroxyl group (Figure 1, group **2c**) and a similar functional pair with an additional water molecule (Figure 1, group **2d**), as well as a lactone H-bonded to the opposite hydroxyl group inside a small internal defect (Figure 1, group **2e**).

In the case of lactones, the relatively wide range of C=O vibration frequencies is determined primarily by interactions with OH groups or water molecules, which can provide their hydrogen atoms for the formation of H-bonds, and not with the carbon skeleton, whose segment directly adjacent to the lactone group is presumably of sp^3 type. The stronger the proton-donor capability of the neighbour, the stronger the frequency decrease, despite the relatively low contribution of the neighbour to VED, for example, when H-bonded to a water molecule, the lactone C=O group contributes about 91% to the vibration at 1754 cm^{-1}. The frequency of a separate lactone group (Figure 1, group **2a**), equal to 1772 cm^{-1}, drops to about 1703 cm^{-1} in the presence of a directly H-bonded OH group, and its contribution decreases to 76%. Note that this value is almost the same for two variants of the relative arrangement of the C=O and OH groups (Figure 1, groups **2c** and **2e**). At the same time, the stretching vibrations of C=O group in the lactone H-bonded to water, regardless of whether the water molecule participates in an additional hydrogen bond with the neighbouring fragment, *e.g.*, OH (Figure 1, groups **2b** and **2d**), are observed in the range of 1740–1755 cm^{-1}, where high absorption is recorded in experiments. It is worth noting that the corresponding H-bonds themselves are relatively weak, judging by the O···H distances from 2.051 to 2.185 Å, and H–O–H bending of the water molecule contributes less than 2% to the VED of vibrational modes. However, when a hydroxyl group, which tends to bind water molecules, is formed close to the carbonyl group of lactone, the latter inevitably participates in hydrogen bonding with water, which will be tightly bound to the GO system due to the hydroxyl group. Therefore, the above-mentioned spectral signature can be considered as a very likely sign of the presence of lactones.

Finally, the carbonyl group can be part of the carboxyl group, where C=O and OH are very close neighbours. A single carboxyl group can be close to other modifying groups, but not form H-bonds with them (Figure 1, group **3a**). Alternatively, the hydroxyl part of the group can be H-bonded to the adjacent ketone group, which should indirectly, due to the redistribution of electron density, affect the carbonyl group (Figure 1, group **3b**). In addition, we considered quite typical situations when the C=O part of the carboxyl group acts as a proton acceptor in the hydrogen bond with the hydroxyl group, namely, when the hydroxyl group is the adjacent edge modifier (Figure 1, group **3c**) or the opposite element in a small defect, an edge modifier that acts as a kind of bridge to another carboxyl group (Figure 1, group **3d**) and a neighbour separated from the carboxyl group by a water molecule, provided that the amount of water is relatively high, so that there may be at least one more water molecule bound to the carboxyl group (Figure 1, group **3e**).

When the carboxyl group is a local modifier of the GO sheet edge and is not associated with other functional groups (Figure 1, group **3a**), its frequency is about 1770 cm^{-1}, and the vibration is localized within the carboxyl group, so that the C=O stretching is coupled to the C–O–H bending, which contribute ~83 and ~6% to the VED, respectively. In the presence of a neighbouring ketone group that coordinates the hydroxyl part of the carboxyl group (Figure 1, group **3b**), the two motions remain coupled, although the latter is transformed into the τ-vibration of the proton in the H-bond of the hydroxyl part orthogonally to the formed H-bond, and they are slightly facilitated due to the partial redistribution of electron density caused by the formation of the H-bond. This is expressed in a decrease in frequency to 1742 cm^{-1} with a decrease in the contribution of C=O to VED to 75% with the contribution of C–O–H unchanged. In both cases, the neighbouring GO skeleton makes almost no contribution to the VED of vibrations, no more than 4%, which means that the motions are localized strongly within the corresponding carboxyl groups. When the external effect becomes direct rather than indirect, that is, when the neighbour forms a hydrogen bond with the C=O part itself, the frequency redshift is very noticeable, namely, in fragment **3c**, shown in Figure 1, the frequency is 1669 cm^{-1}. It seems natural since now it is the bending vibrations of two C–O–H fragments that are coupled to the stretching motion of the carbonyl although estimates show that the contribution of the neighbouring hydroxyl group is about a fifth of that of the hydroxyl that is part of the carboxyl group, *i.e.*, again about 7%. Very similar fractional contributions to the VED of vibration are found when the hydroxyl group, which is directly H-bonded to the C=O moiety of carboxyl, is opposite to the latter within a small structural defect, and the frequency differs by only 5 cm^{-1}, equal to 1674 cm^{-1}. In fact, this observation strongly resembles the above situation seen in the case of ketone groups.

If during deeper oxidation of graphite two carboxyl groups can be formed at the adjacent C sites of the skeleton, so that their C atoms are bound to the C–C–C triangular half of the former C6 ring (Figure 1, group **3d**), then their vibrations are coupled with almost equal weights, namely 44 and 42%. The frequencies of these two vibrations differ by less than 20 cm^{-1} and are close to the value typical for the stretching vibration of C=O in the carboxyl group, which stands apart, namely 1766 and 1783 cm^{-1}. Finally, when a carboxyl group at the edge of a deeply oxidized sample can form hydrogen bonds with water molecules that are presumably present in sufficient quantities in the system (Figure 1, group **3e**), its C=O stretching vibration is characterized by a frequency of 1723 cm^{-1}, which falls within the range characteristic of carboxyl groups H-bonded to hydroxyl neighbours. Note that here one water molecule acts as a link between the carbonyl and hydroxyl parts of the carboxyl group, which enhances the correlation in their oscillations with contributions of 74 and 11% to the VED, respectively. Nevertheless, the total change in the dipole moment for such distortions is expected to be less than that for C=O groups of individual ketone or lactone since the local dipole moments of the CO and OH bonds partially compensate for each other.

Thus, not only the nature of the parent functional group which includes the carbonyl moiety but also the nature of the close proximity of the group affects the frequency of C=O stretching vibration in GO samples. First of all, the ketone C=O vibrations are coupled strongly to the distortions of C=C bonds even in extended segments of the carbon sheet. Therefore, a higher absorption in the spectral range typical of C=C oscillations may indicate a relatively high content of ketone groups directly bound to sp^2 segments. The range typical of the ketone groups adjacent to hydroxyl modifiers of deeply oxidized graphite can be defined as 1590–1620 cm^{-1}, which overlaps with that considered usually as an indicator of the presence of water due to the bending vibrations of its molecules. Thus, only a decrease in the integral intensity of the spectral signal in this range can be attributed to a decrease in

the water content, while the main part of the signal has a different nature. The range of 1740–1755 cm^{-1} can be suggested as typical of the lactone C=O groups that coordinate water molecules. Note that this corresponds to the high absorption of any synthesized GO sample, which may indicate a high actual content of lactone groups. Finally, a much lower absorption in the range of 1670–1720 cm^{-1} can be caused by the excitation of C=O vibrations of carboxyl groups H-bonded to either hydroxyl or water neighbours, and the relative decrease in absorption in this range can be considered as a quantitative measure of the dehydration of carboxyl groups.

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