

Density Functional Theory for Better Understanding Raman Spectroscopy Data of Surface Carbon on Bulk Niobium

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Introduction

Raman microscopy/spectroscopy measurements on Niobium processed according to the recipes for Superconducting Radio Frequency (SRF) cavities show surface patches with relatively thick layers of graphitic carbon¹. Sharp Raman peaks are consistent with graphene or graphite while other broader peaks appear to be disordered or amorphous carbon. Other Raman peaks are consistent with C-H modes from aromatic hydrocarbons.

The purpose of this work is to develop a theoretical framework for understanding the Raman data. The goal is to use Density Functional Theory (DFT) to determine the Raman active vibrational modes of graphene, graphite and amorphous carbon, as well as hydrogen terminated carbon, and to compare with experiment.

Raman Spectroscopy of Niobium

Raman spectra of processed Nb for SRF cavities often display micron-sized patches of graphitic carbon¹, as shown in the two figures below.

Figure 1

Raman Spectroscopy of Nb Surfaces

Surface Carbon Patches on Processed Nb

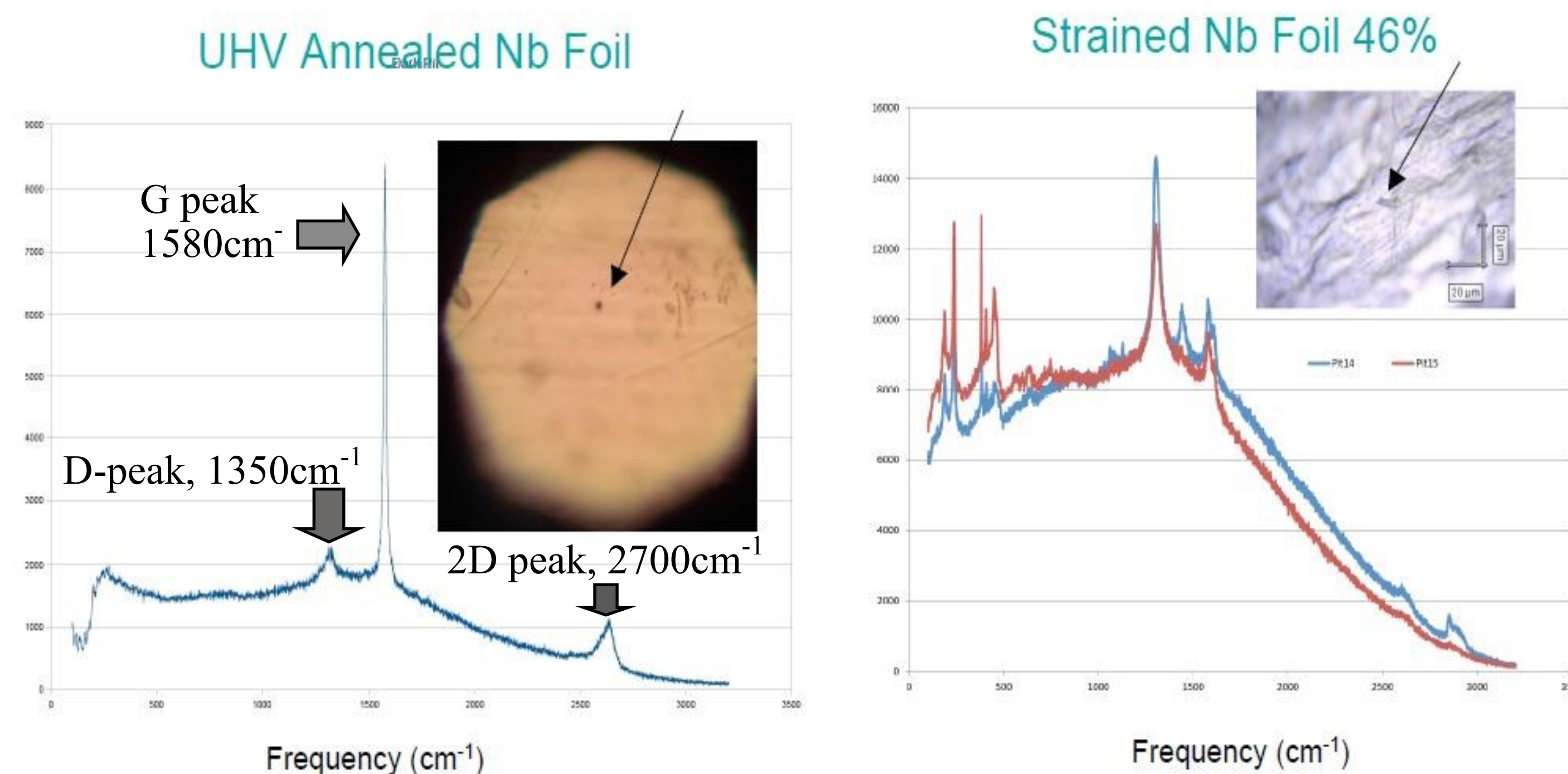


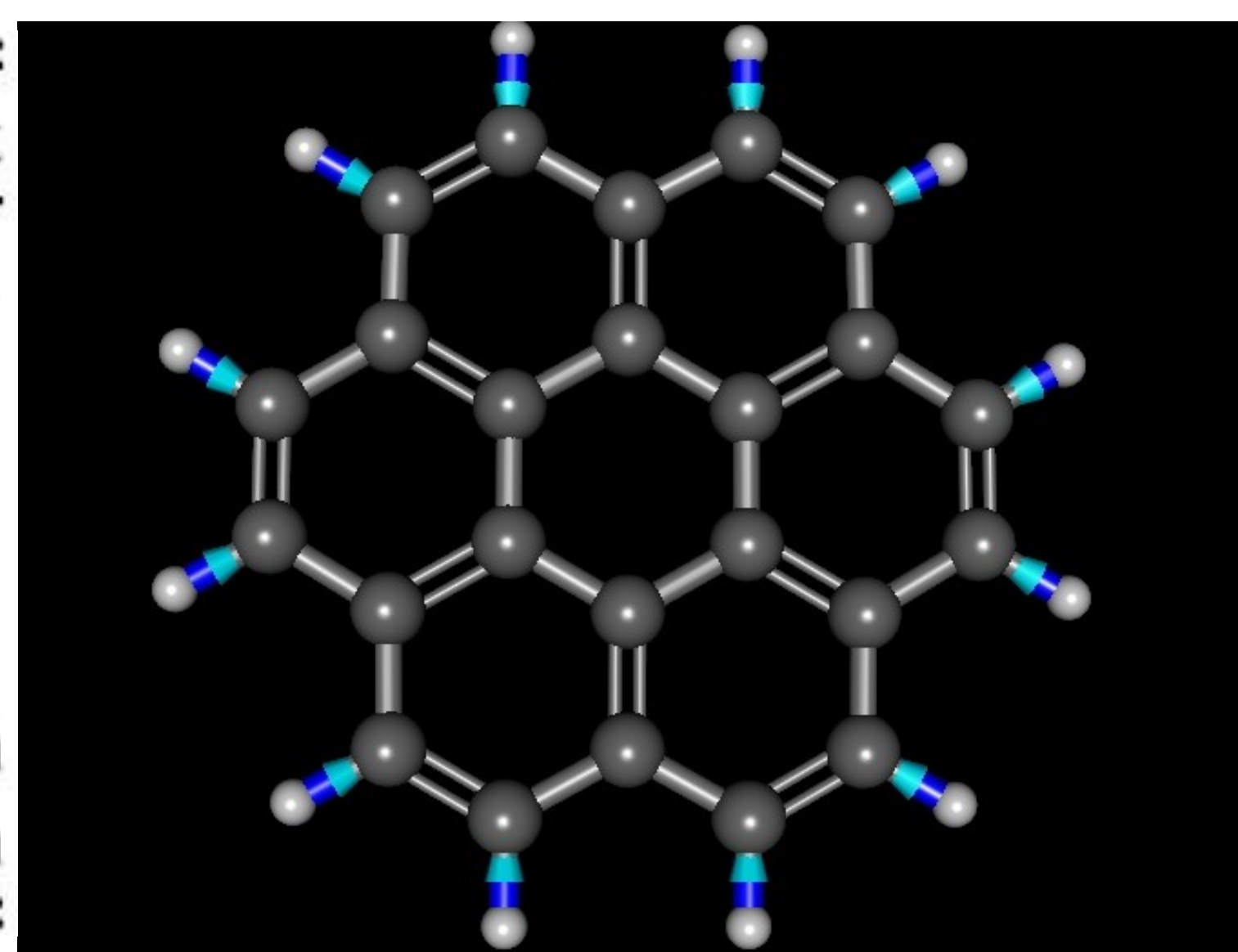
Fig. 1 Representative examples of surface patches of excess carbon (~10 μm) on Nb measured by Raman microscopy/spectroscopy. Left image appears to be that of graphene. Right image shows graphitic modes plus C-H modes near 3000 cm⁻¹. Lower frequency mode near 200 cm⁻¹ and 400 cm⁻¹ have been identified as NbC.

The modes of pit 14 also have graphitic peaks at 1063cm⁻¹, 1129cm⁻¹, 1300cm⁻¹, 1442cm⁻¹, 1582cm⁻¹, 1611cm⁻¹, and 2600cm⁻¹. This pattern is consistent with a combination of the active modes of stearic acid³ and defect-ridden graphene².

Figure 3
Raman active modes of stearic acid, bent Nb foil and their assignments³

Stearic acid (cm ⁻¹)	Nb bent foil (cm ⁻¹)	Assignment
1063	1068	C-C stretch
1130	1140	C-C stretch
1296	1303	C-C twist
1441	1450	CH ₂ bend
1461	1471	CH ₂ bend
2846	2870	CH ₂ stretch
2881	2904	CH ₂ stretch

Figure 2
Molecular movement responsible for 3215cm⁻¹ peak for Coronene



Abstract

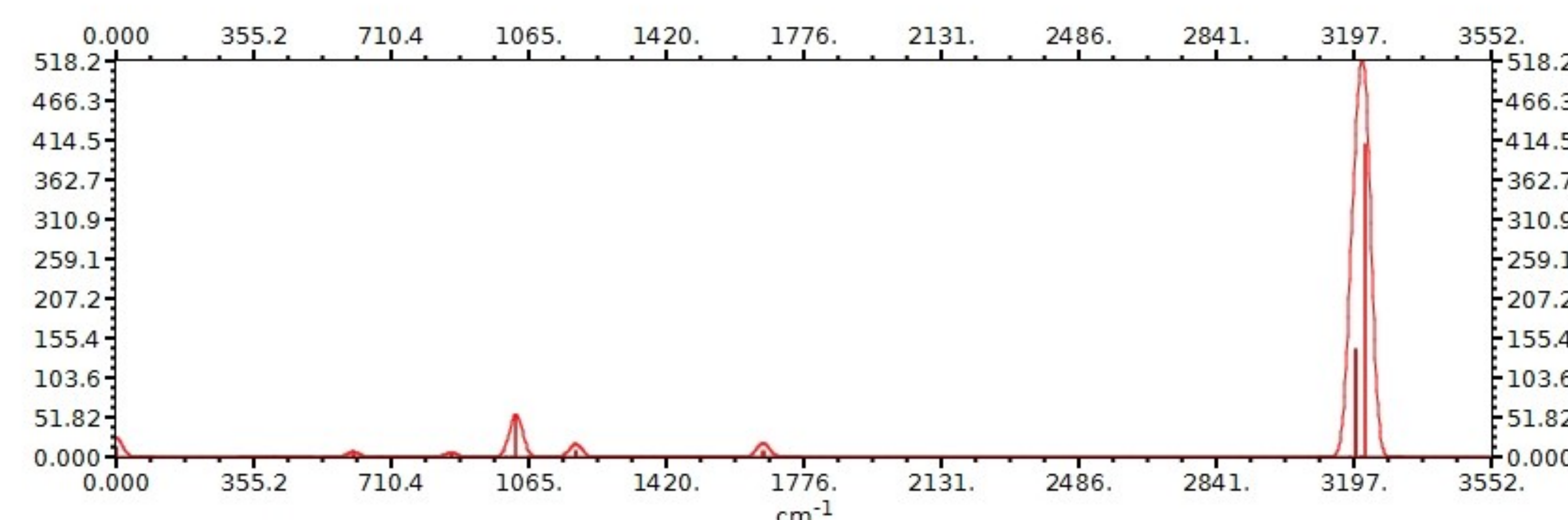
A model of hydrogen-terminated carbon is developed for interpreting carbon-containing systems, such as when Niobium processed for SRF cavities develops layers of graphitic carbon on the surface. A computational comparative study on benzene, naphthalene, and larger aromatic hydrocarbons was performed, giving rise to physical interpretations of observed Raman active modes for hydrocarbons.

Computational Methods

Density Functional Theory (DFT) is a quantum mechanical modelling method that can effectively handle many-body systems such as molecules. It does this by treating the nuclei of the atoms in the system as fixed, and then using functionals of the spatially dependent electron density.

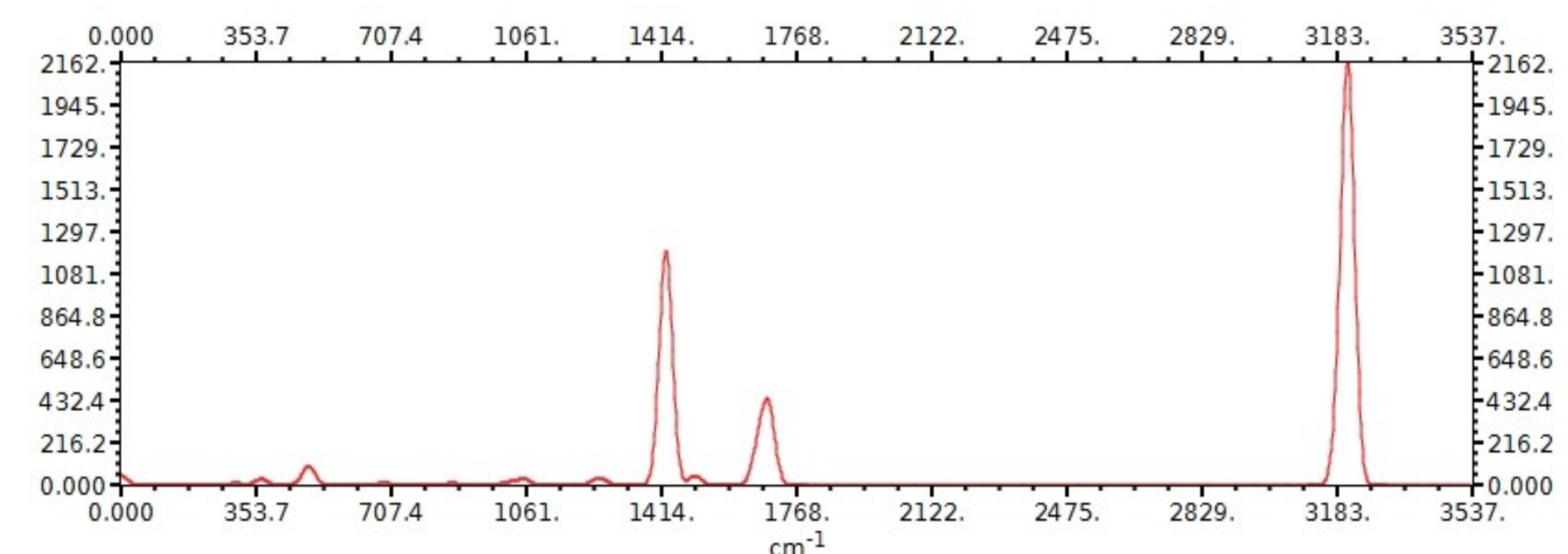
Calculations were performed at the PBE0 level of theory with the cc-pvdz basis set on various polycyclic aromatic hydrocarbons (PAHs). Examples of Benzene and Coronene are shown below.

Figure 4
Computed Raman Modes of Benzene



A major peak is computed at 3229 cm⁻¹, which is known to be the C-H interactions. There are minor peaks at 1035cm⁻¹, 1189cm⁻¹, and 1674cm⁻¹. The latter two were originally attributed to D4 and D' peaks, respectively². The origin of the 1035cm⁻¹ and D4 peaks are in question.

Figure 5
Computed Raman Modes of Coronene



Once again, a large frequency (at 3215cm⁻¹) is computed. In the other aromatic hydrocarbons studied, this peak was found in all of them, between 3200-3250cm⁻¹. Another peak is at 1428cm⁻¹; this peak is found in pit 14 (Fig. 1). Gabedit allows the opportunity to visualize what molecular movement is responsible for this peak, as shown in Fig. 2 on the left. There is another peak at 1670cm⁻¹, attributed to the G peak. Minor peaks at 1057cm⁻¹, 1245cm⁻¹ and 1507cm⁻¹, like stearic acid (Fig. 3).

References

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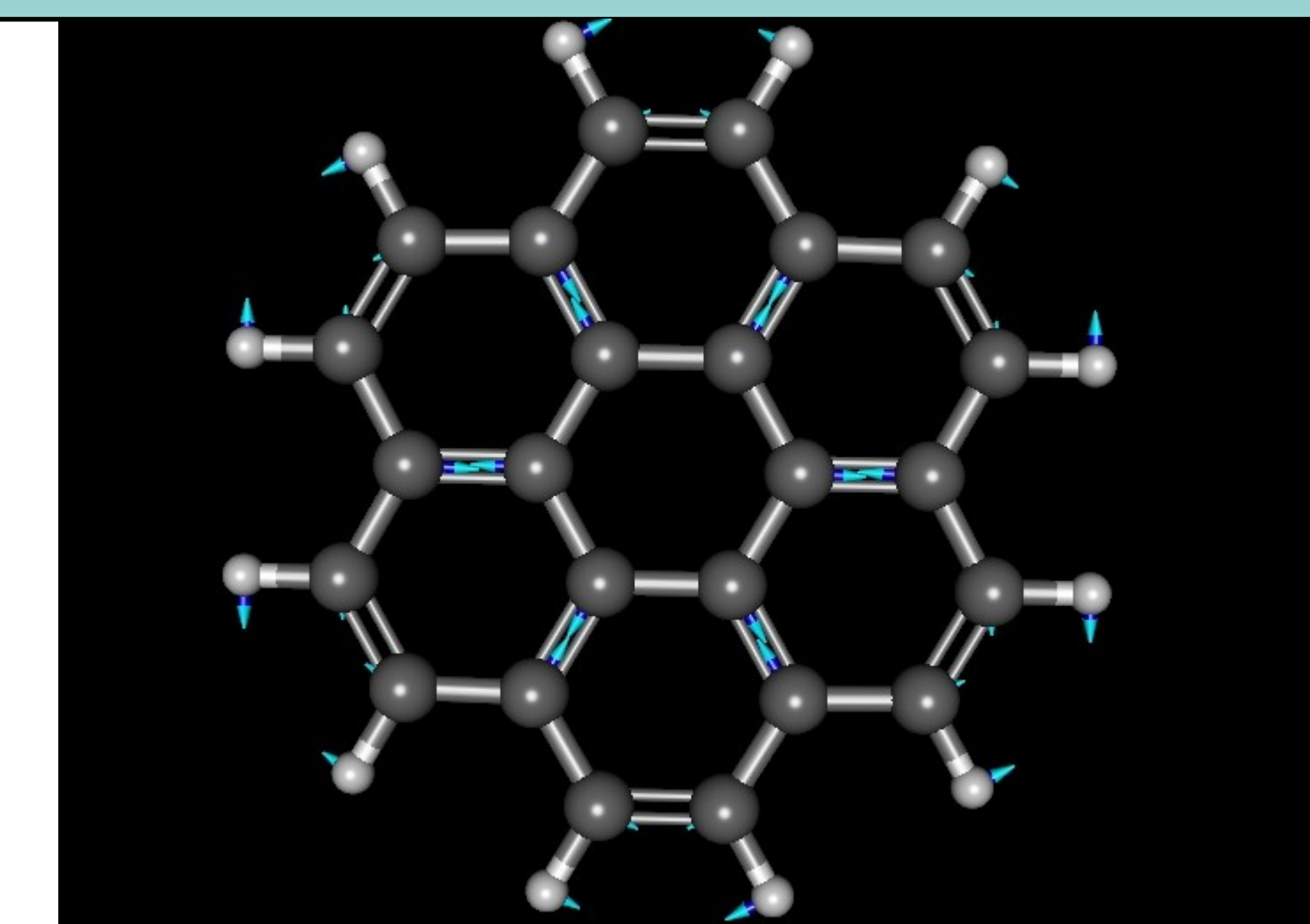


Figure 6
Molecular movement of Coronene at its 1428cm⁻¹ peak, visualized by Gabedit.

Although this motion's computed Raman intensity is quite large relative to the other intensities computed, this C-C double bond interaction is not in the experimental literature for graphene nor Coronene. Due to the direction of the outer atoms' movement, however, it is taken to be one of the various D-modes², just displaced.

Results and Discussion

Gabedit has allowed visualization of modes and therefore the ability to distinguish between C-C and C-H interactions. For example, there is significant C-H bending going on in the vibrational modes seen from 1050cm⁻¹ to 1480cm⁻¹ (such as in Fig. 6 above) for the modeled molecules. The interpretation is that due to the small size and particular shape of the molecules modeled, the C-C stretching that is responsible for the D region peaks can be modified by C-H wagging vibrations on the edge, as found in a similar study done by Ref. [6].

Gabedit has also helped visualize the C-H stretching modes at near 3000cm⁻¹, as seen in Fig. 2.

A comparison can also be made between these modeled molecules, experimental evidence (such as in Fig. 1), and experimental results for stearic acid. On first glance, the peaks in the D region for these PAHs, experimental results, and stearic acid are very similar, such as if one compares Fig. 1, 3 and 5. Because the computed results give more insight into small PAHs, it can be determined that while pit 14's spectrum appears very similar to stearic acid, it is actually composed of PAHs like Coronene.

The D-modes in Coronene appear as Raman active; this is contradictory with current knowledge of graphene's Raman activity. It is suggested that the D-modes in Coronene are appearing as Raman active due to its edge defects - in the form of C-H bonds. It is expected that as PAH molecule size increases, the D-mode computed will be more consistent with experiment, i.e. the computed peak will steadily decrease.

Conclusions and Future Work

- Computations and visualization aids (Gabedit) readily confirm that the Raman peaks at 3000cm⁻¹ and above are C-H stretching modes
- While it is expected that the D-band mode should not be Raman active for pristine graphene, the vibrational mode itself is not found at 1350cm⁻¹ either; instead, it is split up into various split D-bands, in a manner quite similar to Ref. [2].
- PAHs with sizes on the order of Coronene and below can have their Raman spectra in the D band influenced by C-H wagging modes.
- C-H wagging modes can also influence the Raman results
- It is speculated that the D-mode in small PAHs is Raman active due to the C-H bonds ('defects') on their edges.
- With a model comprised of the above observations, it can be concluded that pit 14 in Fig. 1 is composed of small PAHs, in contrast to pit 15, which is more likely composed of larger crystals of amorphous carbon.