# Alkali metal insertion in hard carbon – the full picture<sup>†</sup>

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## Supporting Information

In this Supporting Information further details on the double resonance Raman (DRR) process are given. Moreover, we show that the differences in the vibrational and electronic spectra of the graphitic model structures for Li, Na or K intercalation can be traced back to differences in the resulting layer spacings and not to the particular chemical interaction. Finally, additional Raman spectra for the Na intercalation in hard carbon are shown.

#### The double resonance

Originally, the occurence of the D-band in the Raman spectra of disordered graphite was thought to be related to a symmetry reduction, activating otherwise invisible Raman modes<sup>1</sup>. Only later studies could prove that the D-band intensity actually does not stem from  $\Gamma$ -point phonons, but results from a more complex inter-valley process<sup>2-4</sup>. While defects are found to be a necessary prerequisite for the occurrence of the D-band, it cannot be traced back to a defect-induced activation of previously inactive Raman modes. On the contrary, the D-band is the signature of a socalled double resonance Raman (DRR) process, making certain non-F-point phonons accessible for Raman spectroscopy. In the case of the D-band, the double resonance is a combined process, originating from scattering events between an excited electron, a non–Γ–point phonon and a structural defect. The schematic representation of such a process is depcited in the main text, whereas Fig.1 shows the corresponding Feynman diagram. Here, it should be noted that only the Feynman diagram for one particular DRR process is depicted, while further processes of this kind are also possible (e.g. with a different order of the scattering processes). For the depicted double resonance process, the excitation of an electron from the valence band to an empty state in the conduction band has to be enabled - otherwise the lifetime of an excited state would be negligible and the probability for a DRR process would go to zero. Exciting an electron to an empty state



Fig. 1 Feynman diagram, describing the DRR process with respect to creation and recombination of an electron–hole pair.

in the conduction band, means that the wave length of the laser light, coming from the Raman laser, needs to match the energy difference between initial and excited electronic state. For such a scenario the excited electron can then be shown to have a nonnegligible probability of interacting with the crystal lattice, creating or annihilating a phonon of energy  $\hbar\omega$  via inelastic electron– phonon scattering. Moreover, this kind of process can only occur for particular combinations of energy and momentum transfer between electron and phonon, imposing distinct conditions on the electronic and phonon band structure<sup>4</sup>. Finally, a subsequent elastic scattering event of the electron with a lattice defect is able to scatter the excited electron to a virtual state with momentum close to the original excited state, yet, with a slightly different energy. The electron in this virtual state recombines with the hole it has originally created in the valence band, emitting a photon with reduced/increased wave length, which is due to the energy transfer to/from the excited electron and the created/annihilated phonon. A DRR process has only non-negligible probability if unoccupied states with the right energy are available in the conduction band, lying in the vicinity of reciprocal space high-symmetry points of the electronic band structure (in case of graphite these are the  $\vec{K}$  and  $\vec{K'}$  point).

#### Phonon dispersion curves

In Fig. 2 the phonon spectra for the empty model structure – corresponding to graphite with an AA–stacking – for different layer distances are depicted. The dispersion curves are almost identical, making it evident that the layer distance has no significant impact on the dispersion curves. In particular the G–band is not noticeably affected. This is simply due to the week coupling be-

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Fig. 2 Back–folded phonon dispersion curves of (left) empty (AA-stacking of) graphitic planes with optimized interlayer distance ( $\sim$ 3.6Å), (middle) increased interlayer spacing of 4Å and (right) an interlayer distance that corresponds to that one of the NaC<sub>6</sub> model structure ( $\sim$ 4.5Å). The G–band position is marked by an orange circle.



Fig. 3 Back–folded phonon dispersion curves of a)  $LiC_6$ , b)  $NacC_6$  and AA–stacked graphite with c)  $LiC_6$  and d)  $NaC_6$  geometry and force constants. Only the modes above a certain threshold are shown for better comparison. The G–band position is marked by an orange circle.



Fig. 4 Back–folded phonon dispersion curves of a)  $LiC_6$  with a– and b– axis from  $NaC_6$ , b)  $LiC_6$  with  $NaC_6$  layer spacing and c)  $LiC_6$  with the unit cell size of the  $NaC_6$  structure. Only the modes above a certain threshold are shown for better comparison. The G–band position is marked by an orange circle.

tween the layers.

Similarly, an investigation of AMC<sub>6</sub> type structures has been conducted. First, we compare the back–folded dispersion curves of the optimized structures of  $LiC_6$  and  $NaC_6$ , as depicted in Fig. 3. While the overall appearance of the dispersion curve is similar,

the G–band (the high frequency  $\Gamma$ –point phonons at ~1200 and ~1350 cm<sup>-1</sup>, respectively) is significantly further downshifted in case of NaC<sub>6</sub>. To disentangle the impact of the intercalated ion (Li/Na) from changes in the carbon layers, we have taken the LiC<sub>6</sub> and the NaC<sub>6</sub> structure and removed the intercalated ions,



Fig. 5 Back-folded electronic band structure for LiC<sub>12</sub>, (left) and NaC<sub>12</sub>, (middle) and for LiC<sub>12</sub> with fixed NaC<sub>12</sub> geometry and fixed atomic positions.

while keeping the force constants for the C–C interaction that were obtained when the intercalated ions were included. When comparing panel a) and c) as well as b) and d), we realize that only at low frequencies the dispersion is changed. This indicates that the unchanged modes are not directly affected by the intercalated ion.

On the other hand, we observe differences between  $\mathrm{Li}\mathrm{C}_6$  and NaC<sub>6</sub>. To better understand these differences we have investigated further LiC<sub>6</sub> model structures with different geometries. In Fig. 3a) the dispersion curve for a  $LiC_6$  structure with a- and baxis as in  $NaC_6$  and the c-axis corresponding to  $LiC_6$  is depicted. The resulting dispersion is almost identical to that one of optimized LiC<sub>6</sub>. At the same time panel b) shows the dispersion for LiC<sub>6</sub> with the c-axis increased to that one of NaC<sub>6</sub>. Now, significant changes can be observed, while the resulting dispersion is actually very close to that one of NaC<sub>6</sub>; this is in particular visible for the G-band. In panel c) the dispersion for LiC<sub>6</sub> with full NaC<sub>6</sub> geometry is depicted. Again, the dispersion is almost identical to the NaC<sub>6</sub> dispersion. Thus, we observe a significant impact of the c-axis parameter. At first glance, this comes as a surprise, since for intercalation-free carbon layers we could not observe significant changes in the dispersion with changing layer distance. In fact, these contrasting findings can only be reconciled by differences in the charge transfer to the carbon planes that affect the C–C bond strength and the associated vibrations. In other words, the layer distance affects the charge transfer from the intercalated ion to the carbon layers. Hence, in this perspective the shifting of the G-band can actually be interpreted as an electronic effect. This interpretation is also confirmed by Bader analysis, where we find less positive Li charges with increasing layer distance.

## Electronic structure

In Fig. 5 the back–folded electronic band structure for different  $\text{LiC}_{12}$  model structures and for  $\text{NaC}_{12}$  is depicted. While the fully optimized  $\text{LiC}_{12}$  structure shows degenerate bands at the K–point in case of  $\text{NaC}_{12}$  the degeneracy is lifted. Indeed, this difference originates from the different layer spacings of full and empty layers. In case of Na intercalation the Na–containing layers have a spacing of ~4.5Å, while the Na–free layers are only ~ 3.3Å apart. For LiC<sub>12</sub> on the other hand, the layer distances for Li–containing

and Li–free layers are  $\sim$ 3.7 and  $\sim$ 3.3Å. For this small differences the electronic states for emtpy and filled layers still fall on top of each other. However, when LiC<sub>12</sub> is calculated within the NaC<sub>12</sub> lattice and for fixed atomic positions, the resulting back–folded band structure resembles that one of NaC<sub>12</sub>. Hence, the differences in the back–folded band structure can again be traced back to the layer spacing.

## Additional Raman spectra for the plateau region

In Fig. 6 further Raman spectra for the Na intercalation in hard carbon are shown. All depicted Raman spectra were obtained for the plateau region at low potential. It is clearly visible that the spectra remain essentially unchanged, in particular the G–band position is not affected by further Na insertion.



Fig. 6 Raman spectra for the plateau region as observed for the Na intercalation in hard carbon.

#### Notes and references

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