Single-atom vibrational spectroscopy in the STEM

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For defects in crystal, there are two types of vibration modes:

**Localized mode**
- vibration frequencies above maximum frequency of the host.
- its eigenvector is localized on defect

**Resonant mode**
- vibration frequencies within the frequency of the host.
- its eigenvector is spatially extended

Resonant modes are also called *quasi-* or *pseudo-localized modes*, for vibration amplitude of the impurity is large.

Vibrational STEM-EELS has emerged as a powerful tool for probing the vibration response of material with high spatial resolution.
By adjusting deflectors, the EELS entrance aperture and the bright field disc was not overlap.

The off-axis geometry suppresses the relative contribution of elastic scattering and delocalized phonon scattering, favoring localized impact phonon scattering.
EELS of Si impurity in graphene

**EELS & STEM images of single Si impurity**

- Blue & red curves are EELS of pristine graphene (Gr) and single Si impurity, respectively, obtained from blue and red square.

- The differences of EELS above ZLP (marked by arrow) was caused by the different phonon scattering probability of graphene and Si impurity.
EELS of Si impurity in graphene

➢ **Zoomed in EELS of Gr & Si impurity**

- Energy loss peak of Gr at 85 meV & 170 meV was attributed to scattering of LA/TA and LO/TO modes.

- The differential EELS (Si-C, black line) reflects the change of phonon scattering probability.

➢ **Experiment differential EELS vs the calculated results**

- The calculated differential EELS was obtained by:
  \[
  \tilde{n}(\omega) = \left[ n^{Si}(\omega) + 3n^{C1}(\omega) - 4n^{bulk}(\omega) \right]/4
  \]
  
  \(n^X(\omega)\) is projected phonon DOS of X atom.

- All main feature peaks are consistent.
Localization of single Si impurity’s vibrational mode

➢ In-plane projected phonon DOS (PPDOS) vs EELS at different site

- Only the in-plane component of PPDOS is relevant to the vibration spectrum.
- The PPDOS of Si impurity & neighboring C atoms indicate the vibration modes of Si impurity possess a degree of localization.
- The EELS obtained at different atomic position is consistent with the PPDOS.
Resonant mode in Si@Gr

➢ In-plane Si PPDOS calculated by 13-atom fragment

![Graph showing Si PPDOS with wavenumber and energy loss on the x-axis and Si component on the y-axis.]

- The results are consistent with the that calculated by large supercell.

➢ Inverse participation ratio (IPR) of Si@Gr

- IPR~1 , localized; IPR~1/N , delocalized.
- Vibration mode of Si is delocalized, but the Si component is enhanced.

- The resonant mode caused by the hybridization of local impurity modes with vibrational continuum of the Gr bulk.
Conclusions

- A vibrational STEM-EELS, which is able to probe the vibration of single-atom impurity was developed.

- The vibration mode of single Si impurity in graphene possesses a degree of localization.

- The vibration mode of single Si impurity is resonant mode, which caused by the hybridization of local impurity modes with vibrational continuum of the Gr.