Second harmonic generation in strained monolayer transition metal dichalcogenides

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Material response to an external field

**linear optics:**
the response of a crystal to an electric field \( F \) depends linearly on the field

\[
P(\omega) = \chi^{(1)}(\omega) F(\omega)
\]

**nonlinear optics:** with increasing field strength, higher orders can be important

\[
P_{\omega} = \chi^{(1)}(\omega_0) F_{\omega_0} + \chi^{(2)}(2\omega_0) F_{\omega_0} F_{\omega_0} + \chi^{(3)}(3\omega_0) F_{\omega_0} F_{\omega_0} F_{\omega_0} + \ldots
\]
Second harmonic generation (SHG)

amplitude:

$$\chi^{(3)} F^3 \ll \chi^{(2)} F^2 \ll \chi^{(1)} F$$

but...

symmetry!

$$P(F) = \chi^{(1)} F + \chi^{(2)} F^2 + \chi^{(3)} F^3 + \cdots$$

$$P(-F) = -\chi^{(1)} F + \chi^{(2)} F^2 - \chi^{(3)} F^3 + \cdots = -P(F)$$
Importance of SHG?

• Radiation source
  ▪ coherent light at higher frequency

• Diagnostics
  ▪ surface sensitive technique to analyze properties of materials
  ▪ analyze change of electronic and crystal structure
    ⇒ strain mapping in 2D materials
Transition metal dichalcogenides (TMDs)

2D materials
- graphene (semi-metal)
- hBN (insulator)
- TMDs (semiconductor)

TM = Mo, W, etc.
D = S, Se, Te

Strain mapping in TMDs
A model for strained TMDs

PRISTINE

\[ P_i = \chi^{(2)}_{ijk} F_j F_k \]

STRAINED

\[ \chi^{(2)}_{ijk} = \chi^{(2,0)}_{ijk} + \frac{\partial \chi^{(2)}_{ijk}}{\partial u_{lm}} u_{lm} \]

\( u_{lm} \) ... strain tensor

photoelastic tensor

\[ p_{ijklm} = \frac{\partial \chi^{(2)}_{ijk}}{\partial u_{lm}} \]

• 2\(^3\) components
• 4 non-vanishing
  \( \chi_{xxx} = -\chi_{xyy} = -\chi_{yxy} = -\chi_{yyx} = \chi_0 \)
• 1 independent parameter \( \chi_0 \)

• 2\(^5\) components
• 12 non-vanishing
• symmetry: 2 independent parameters \( p_1 \) and \( p_2 \)
Experimental idea

apply controlled strain
$\epsilon_{aa}, \epsilon_{bb}, \chi_0$ known

measure SHG

get $p_1, p_2$

map elastic strain in an arbitrarily oriented sample
$\epsilon_{aa}, \epsilon_{bb}$

First principles calculation

- long wavelength limit
- independent particle approximation (IPA)
- neglect local field effects

\[ \mathcal{H}(t) = \frac{1}{2} \sum_i [p_i^2 + V_{KS}(x_i)] + \sum_i p_i \cdot A(t) \]

\[ F(t) = -\frac{1}{c} \frac{\partial}{\partial t} A(t) \]

\[ \chi^{(2)}(-2\omega; \omega, \omega) \propto \sum_{nm} \int \frac{d\mathbf{k}}{\omega_{nm}(\mathbf{k}) - 2\omega} \left[ \frac{f_{nl}r_{nm}(\mathbf{k})r_{ml}(\mathbf{k})r_{ln}(\mathbf{k})}{\omega_{ln}(\mathbf{k}) - \omega} + \frac{f_{ml}r_{nm}(\mathbf{k})r_{ml}(\mathbf{k})r_{ln}(\mathbf{k})}{\omega_{ml}(\mathbf{k}) - \omega} \right] \]

\[ \omega_{nm} = \omega_n - \omega_m \quad \text{... transition energy} \]
\[ f_{nm} = f_n - f_m \quad \text{... difference in occupation} \]
\[ r_{nm} \quad \text{... dipole matrix element} \]

used as implemented in the exciting-code [1,2]

Strongest transition amplitude in regions of the Brillouin zone where the bands are parallel (band nesting)

This is also where the bands change strongly under strain

vacuum = 18 Å
k = 70×70×1
n\textsubscript{unocc} = 40
R\text{G}_{\text{max}} = 10.0
Sensitivity of the SHG signal to strain

**Experiment**

\[ 2\omega = 3.1 \text{ eV} \]

Very strong change with strain

**Simulation**

\[ 2\omega = 2.62 \text{ eV} \]

Same qualitative trend
Verification of the photoelastic tensor description

comparison fit \((p_1, p_2)\) and simulation \(2\omega=2.62\) eV

... but exhibits a strong energy dependence

linearization of \(\chi^{(2)}\) works well...
Origin of the energy dependence

$$\omega = \epsilon_{ck} - \epsilon_{vk}$$

$$\text{joint density of states}$$

$$\text{JDOS}(\omega) \propto \sum_{vck} \delta (\omega - (\epsilon_{ck} - \epsilon_{vk}))$$

details of the directional dependence from dipole moments $r_{nm}$
Effects of strain at different energies

- peaks shifted to lower energies
- changes shape of the peaks
- shifts resonances in k-space

Strongest response to strain can be expected on the edges of the excitation peak

Current measurements at fixed energies ⇒ energy dependent measurements are in preparation
conclusion

- strain mapping via SHG is an excellent tool for strain measurements in TMDs
- a tunable laser will be needed due to the energy dependence of the photoelastic tensor
- best resolution can be achieved on the rising and falling edges of the signal
  ⇒ this is also where the photoelastic tensor description can be applied

outlook

- compare to experimental energy-dependent data
- beyond IPA: inclusion of local field and excitonic effects

THANK YOU