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RIXS studies on Two-dimensional Magnetic Materials

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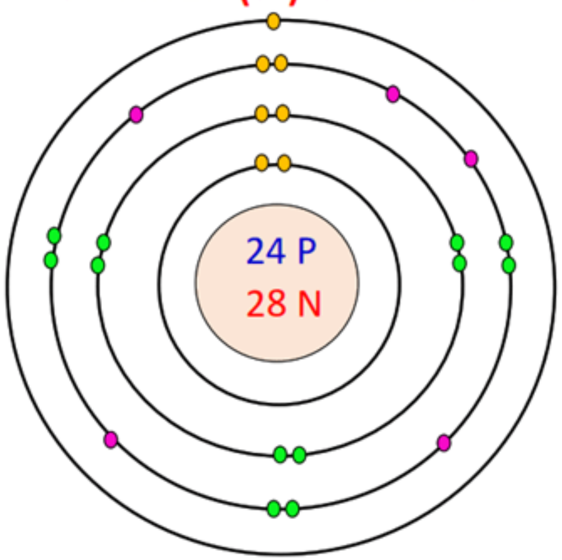
What is Spin :

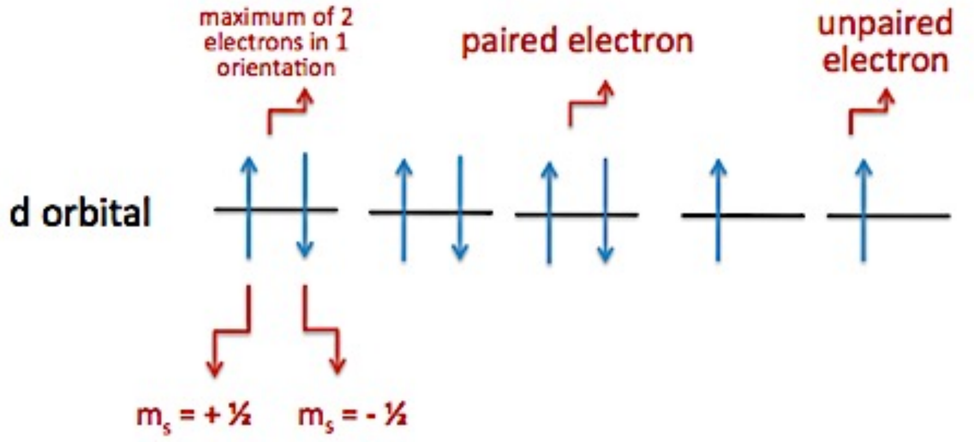
24
Cr
Chromium

Chromium (Cr) Bohr Model

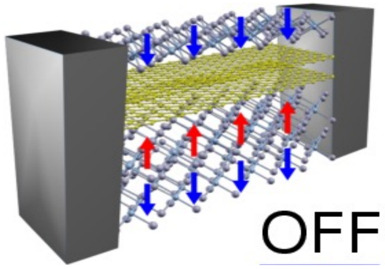


[2,8,13,1]

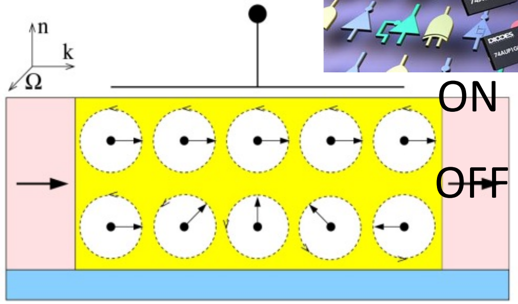
$$Cr \Rightarrow \; 1s^2\; 2s^2\; 2p^6\; 3s^2\; 3p^6\; 4s^1 3d^5$$



Applications

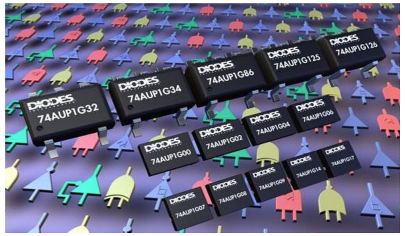


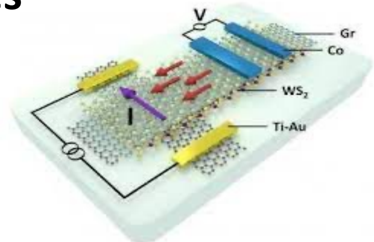
Spin valves



SFET

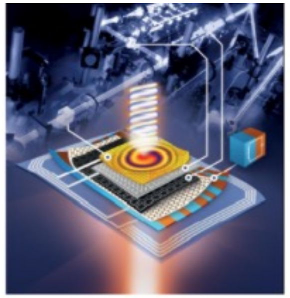
Spin logic switches





Spin transistors

Optical modulators



Valleytronics

What is Spin :

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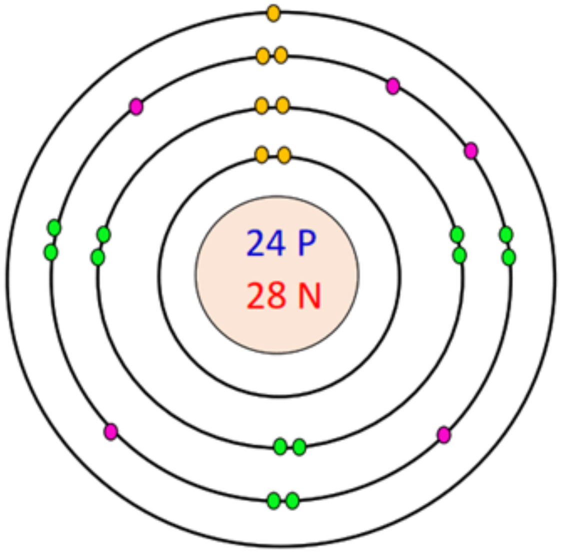
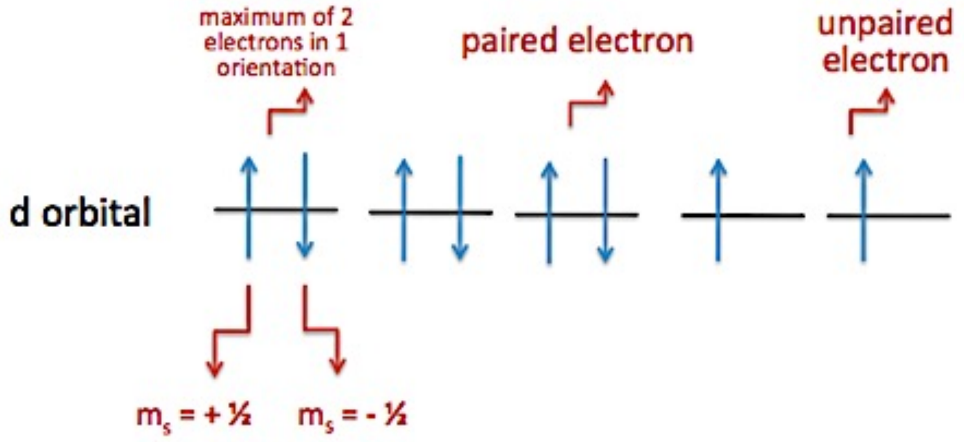
Chromium (Cr) Bohr Model

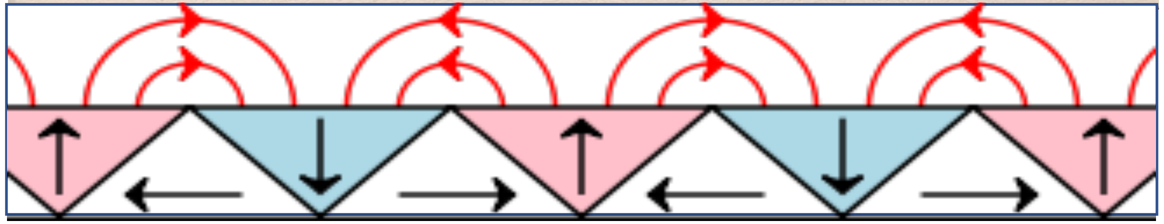


[2,8,13,1]

$$Cr \Rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^5$$

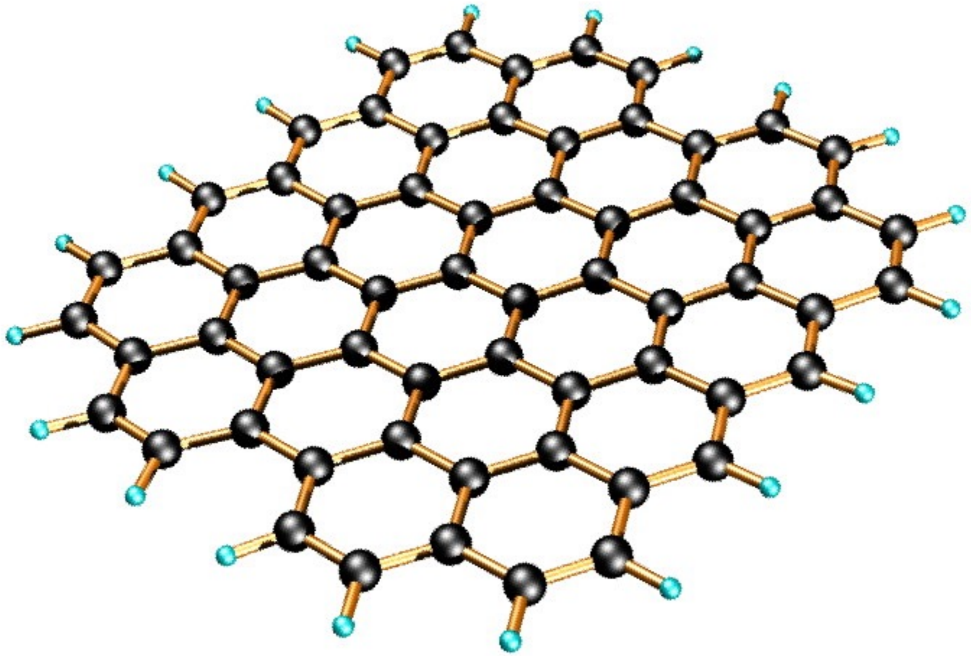


Fridge Magnets



Two-dimensional (2D) van der Waals (vdW) materials :

In 2004, graphene was fabricated via scotch tape exfoliation ;

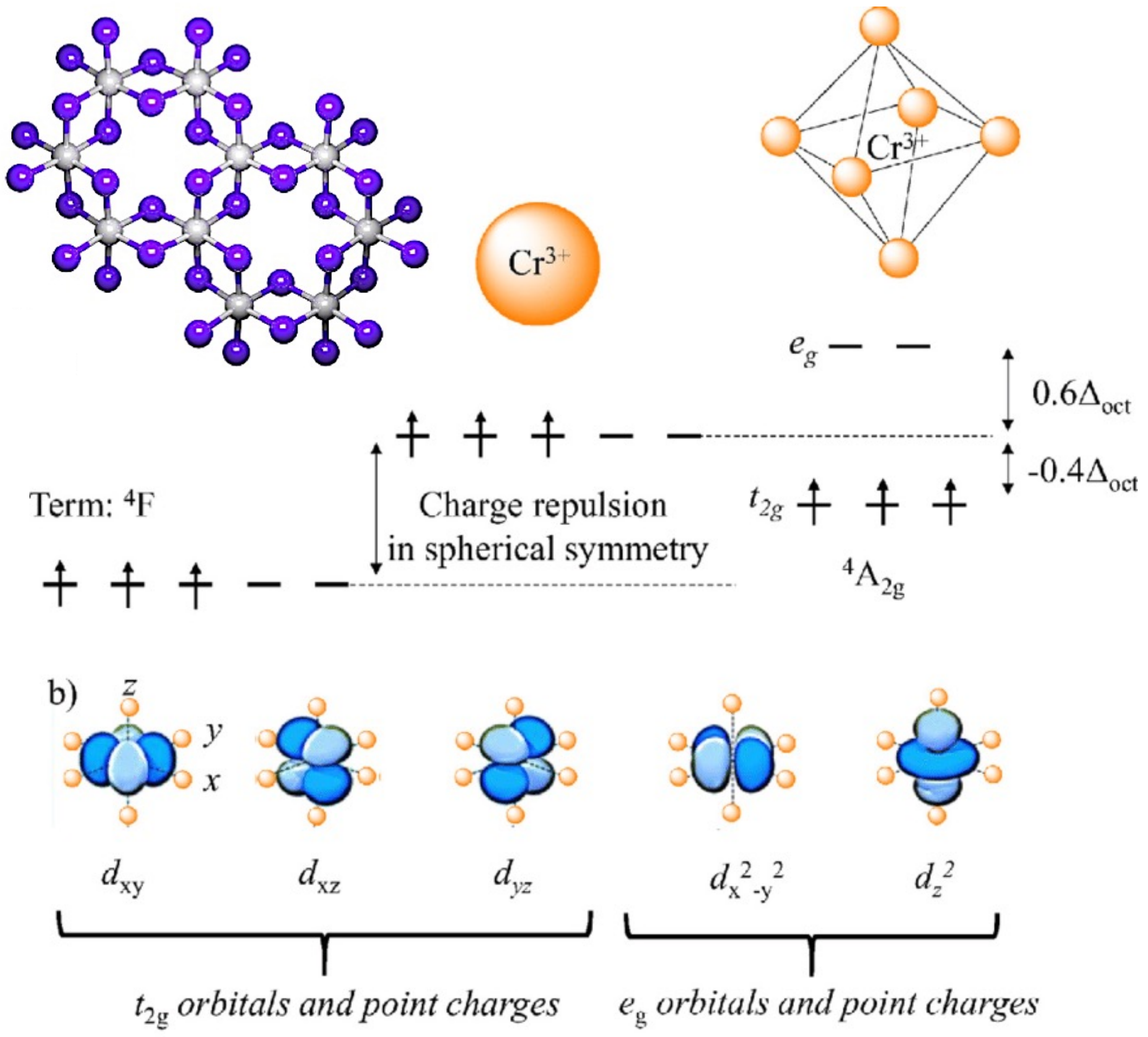


Crystal structure of graphene[1]

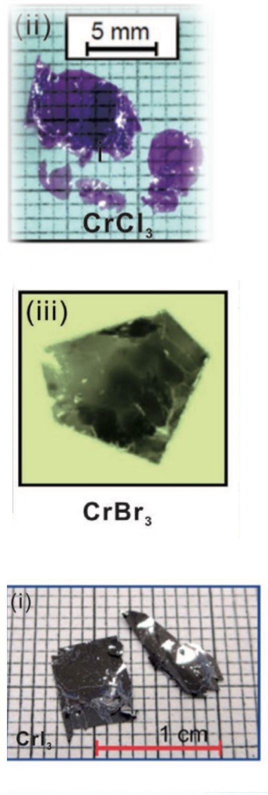
- First Two-Dimensional (2D) semiconductor material
- Layered material arranged in a honeycomb-like pattern
- Unique structural, mechanical and electronic properties
- Shows magnetism in ground states

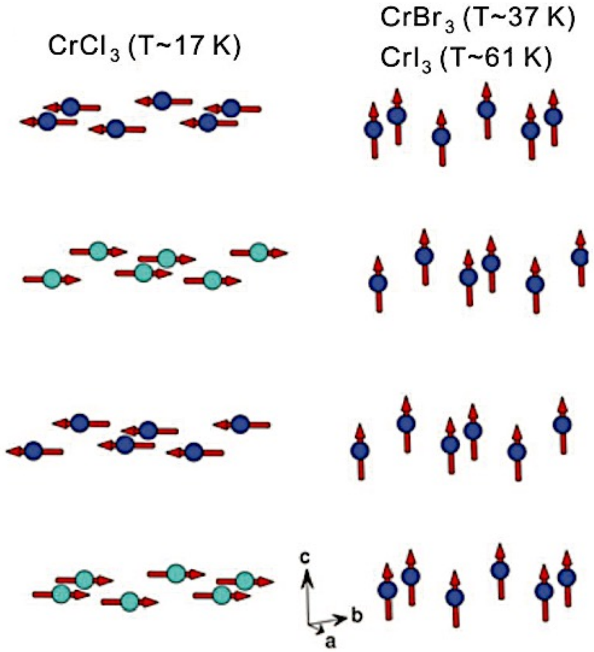
As a result of finding other layered materials, Magnetism up to monolayer in CrI_3 was discovered in 2017.[3]

Chromium Trihalides CrX_3 (X = Cl, Br, I):



- Layer dependent magnetism
  - monolayer – Ferromagnetic (FM)
  - bilayer – Antiferromagnetic (AFM)
  - bulk - $CrCl_3$ – AFM, $CrBr_3$ – FM, CrI_3 – FM



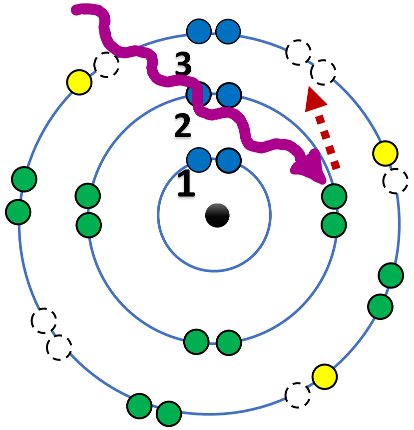


- Crystallographic phase transitions
  - $CrCl_3$ – 240 K
  - $CrBr_3$ – 420 K
  - CrI_3 – 200 K

X-Ray Absorption (XAS) and X-Ray Emission (XES) Spectroscopy:

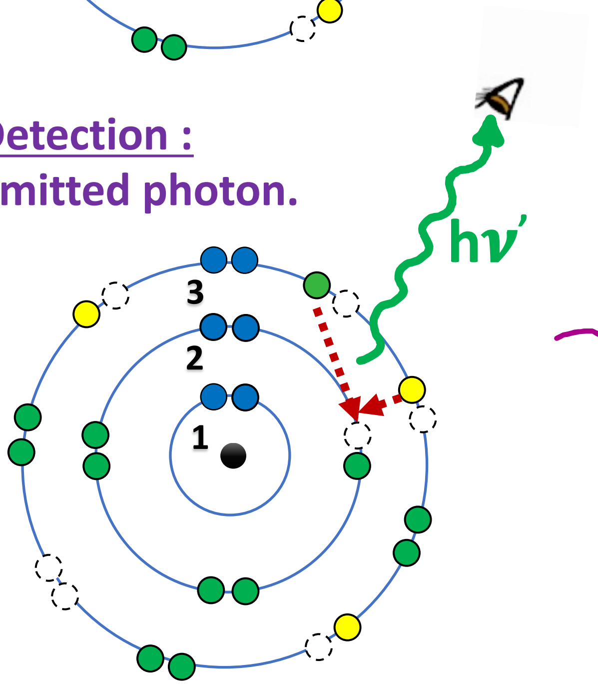
Incidence :

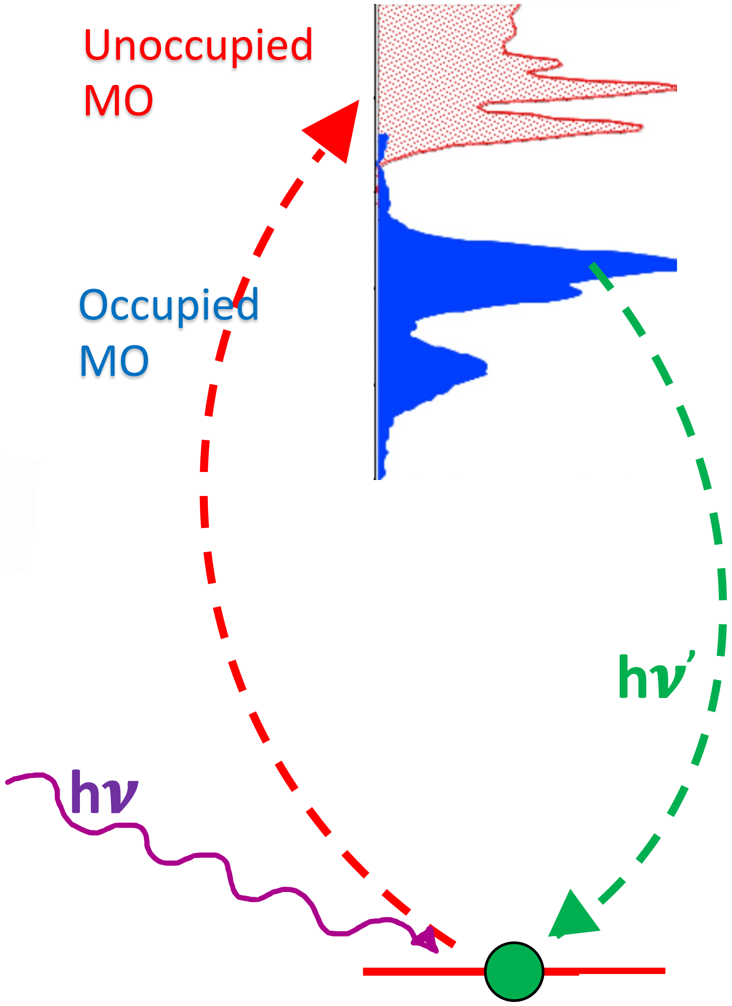
tunable photon



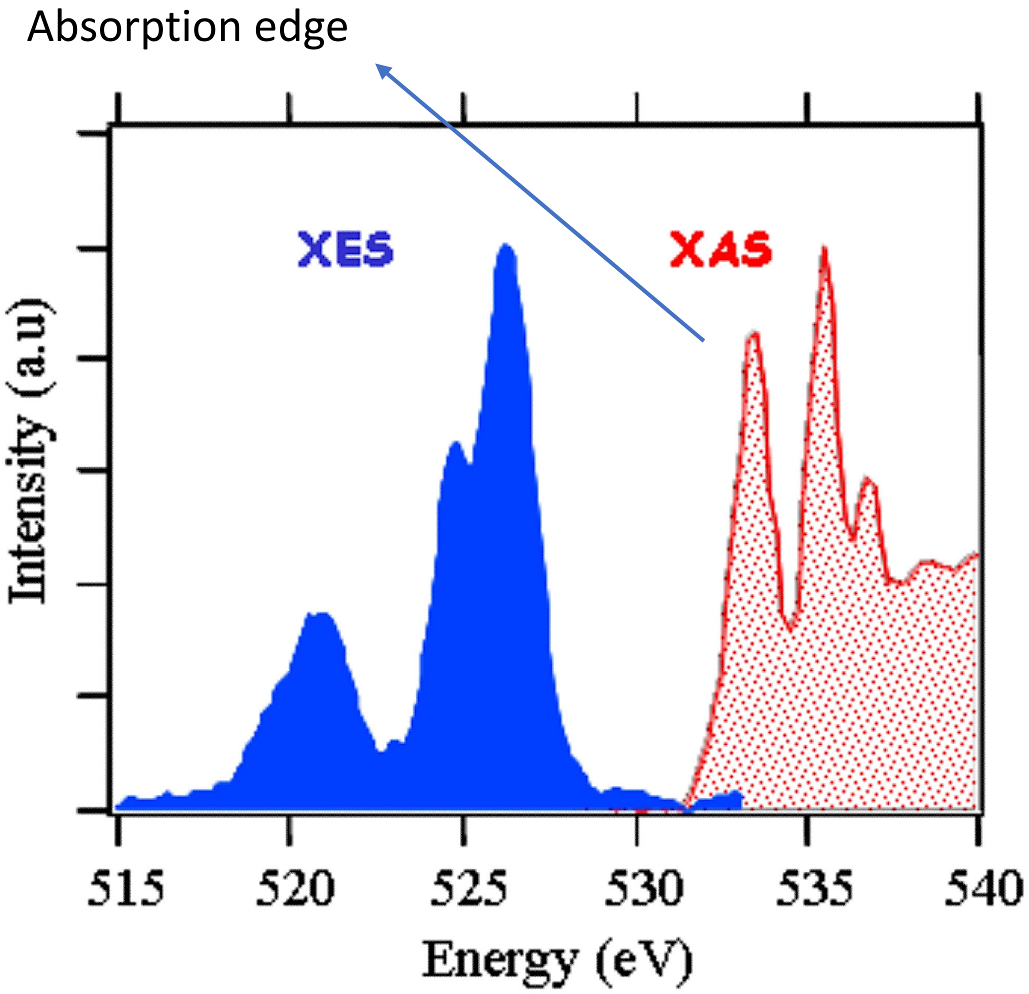
Detection :

Emitted photon.



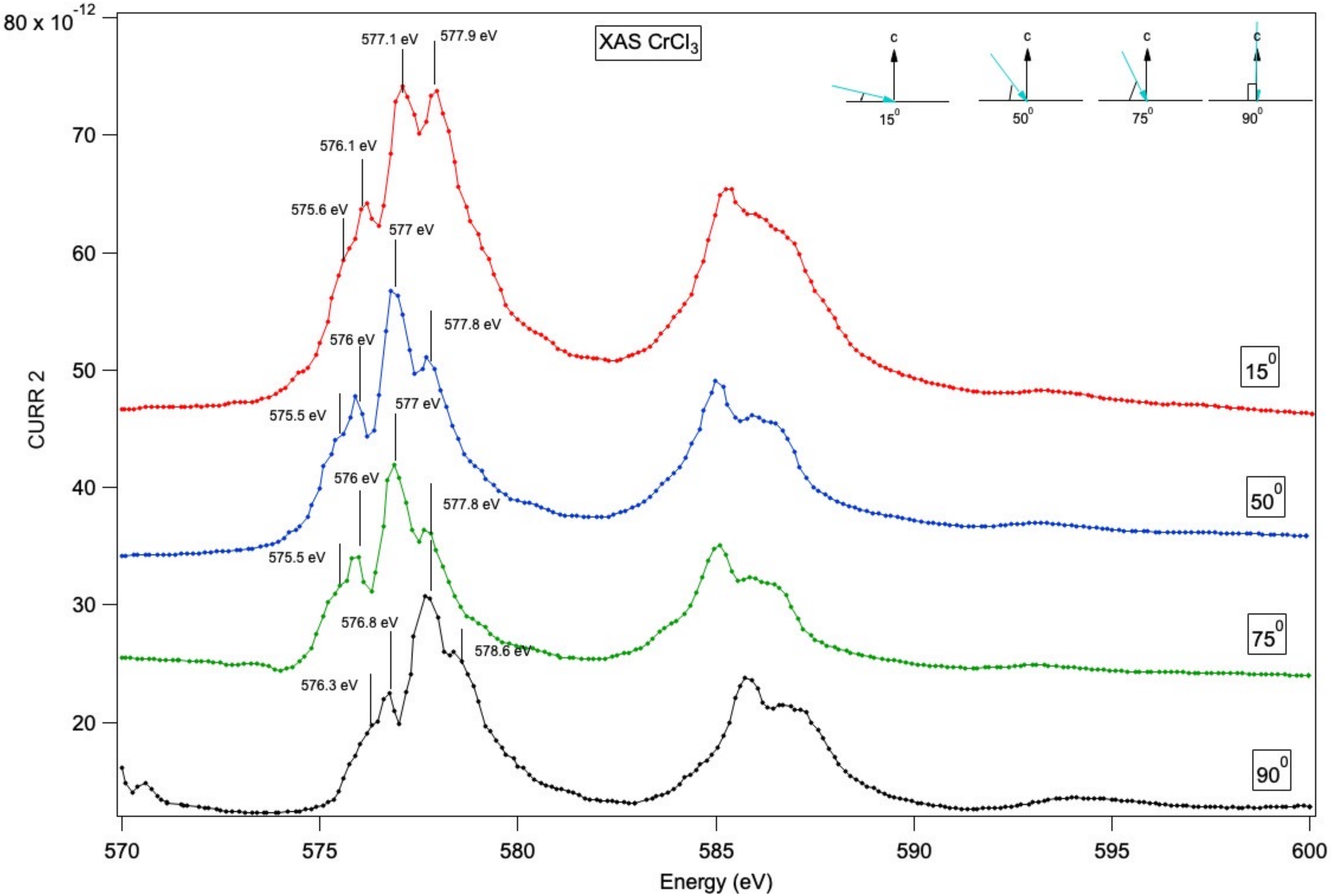


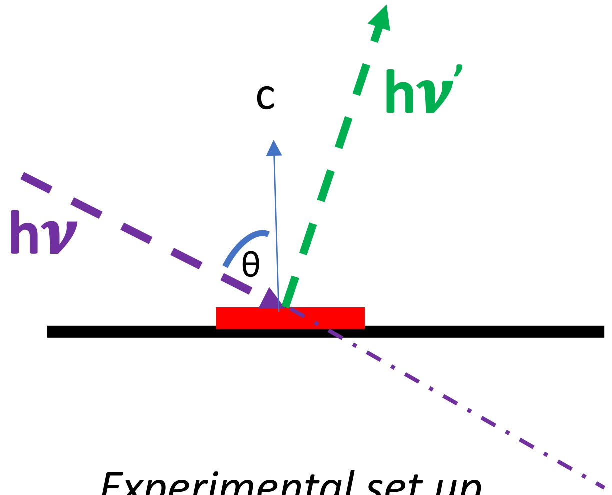
$2p^6\ 3d^3$ -> $2p^5\ 3d^4$ -> $2p^6\ 3d^3$



1. *Soft-x-ray spectroscopy probes nanomaterial-based devices*
2. *J. Am. Chem. Soc., 128, 5001 (2006).*

X-ray Absorption Spectroscopy :





Experimental set up

RIXS measurements on CrX_3 (X=Cl, Br and I) :

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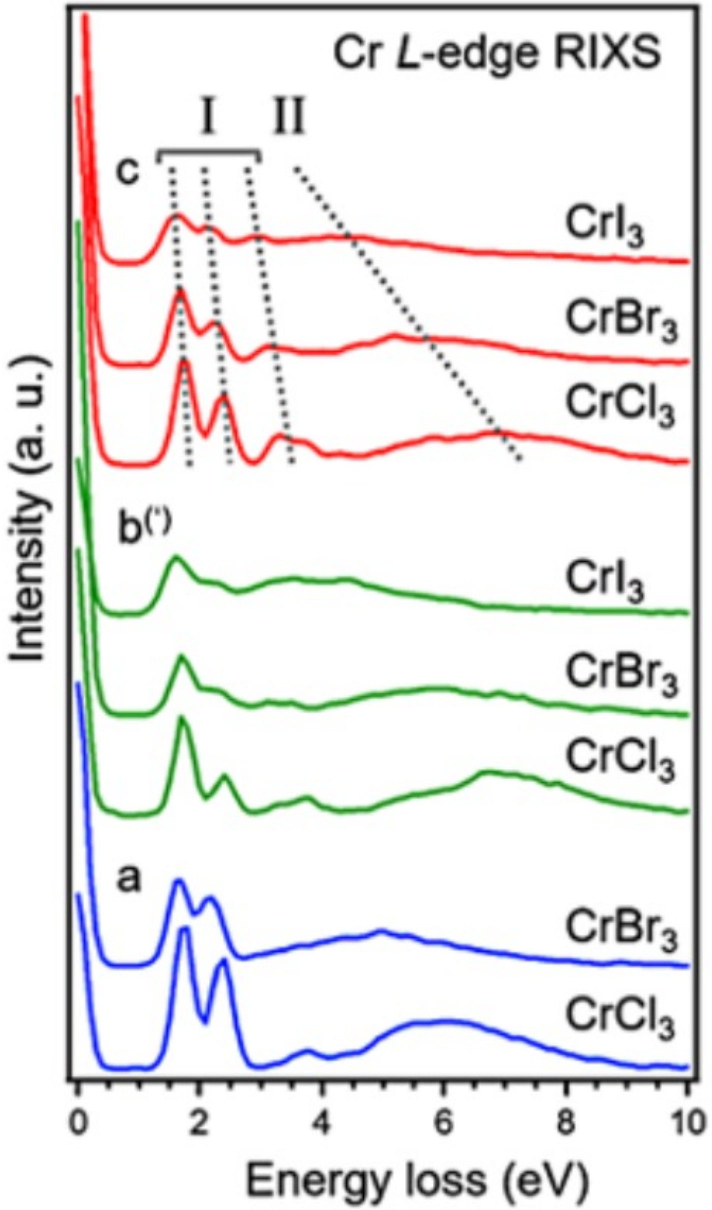
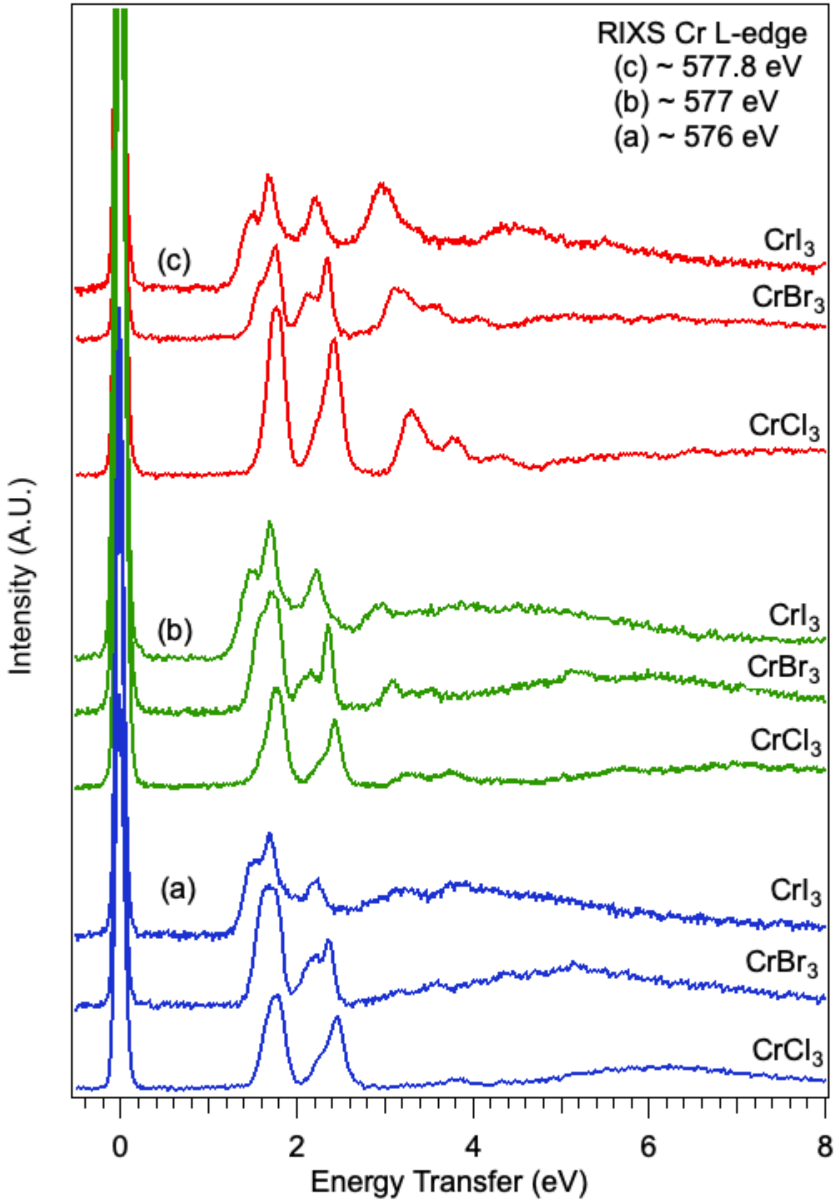


Preliminary RIXS Data:
From Advanced Light Source
Res. ~0.3 eV

High Resolution data:
BESSY II
Res. ~120 meV



Atomic Multiplet Calculation (Quanty) :

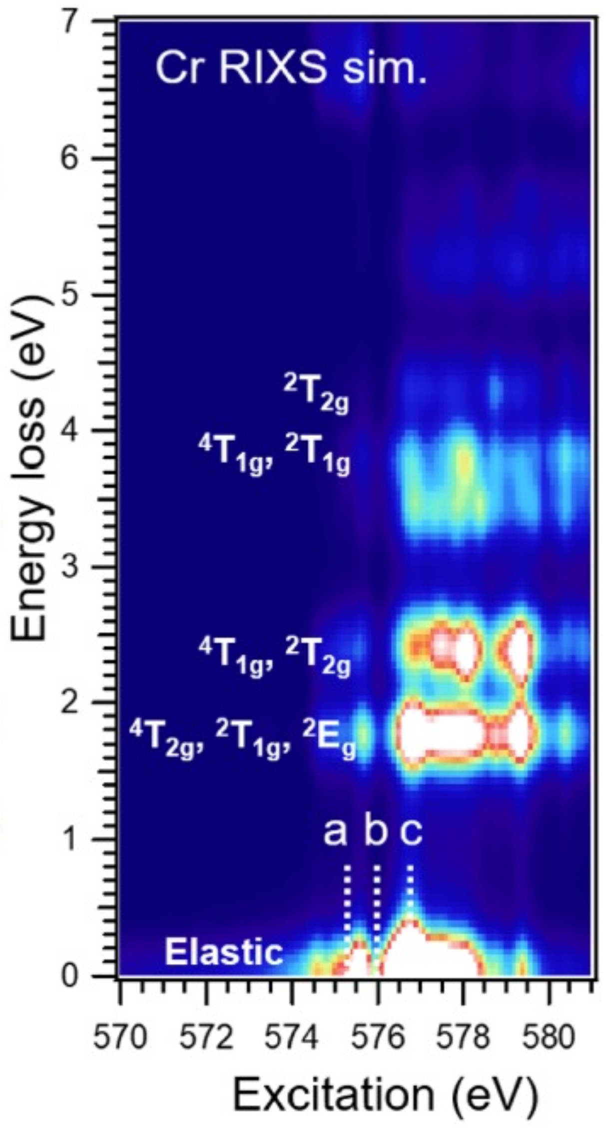
- Quanty is a many body script language and it can be used to simulate core electron spectroscopies such as XAS, XES, RIXS, ELD etc.
- For CrX_3 system, multiplet ligand field theory was used in the XAS and RIXS simulations.
- In quanty simulations, the basis sets are used for the Fermionic modes and Bosonic nodes (molecular orbitals from Hatree-Fock calculations)

$$NF = 20 \;\; --\textit{Number of spin orbitals}$$
$$NB = 0 \;\; --\textit{Number of phonon modes}$$

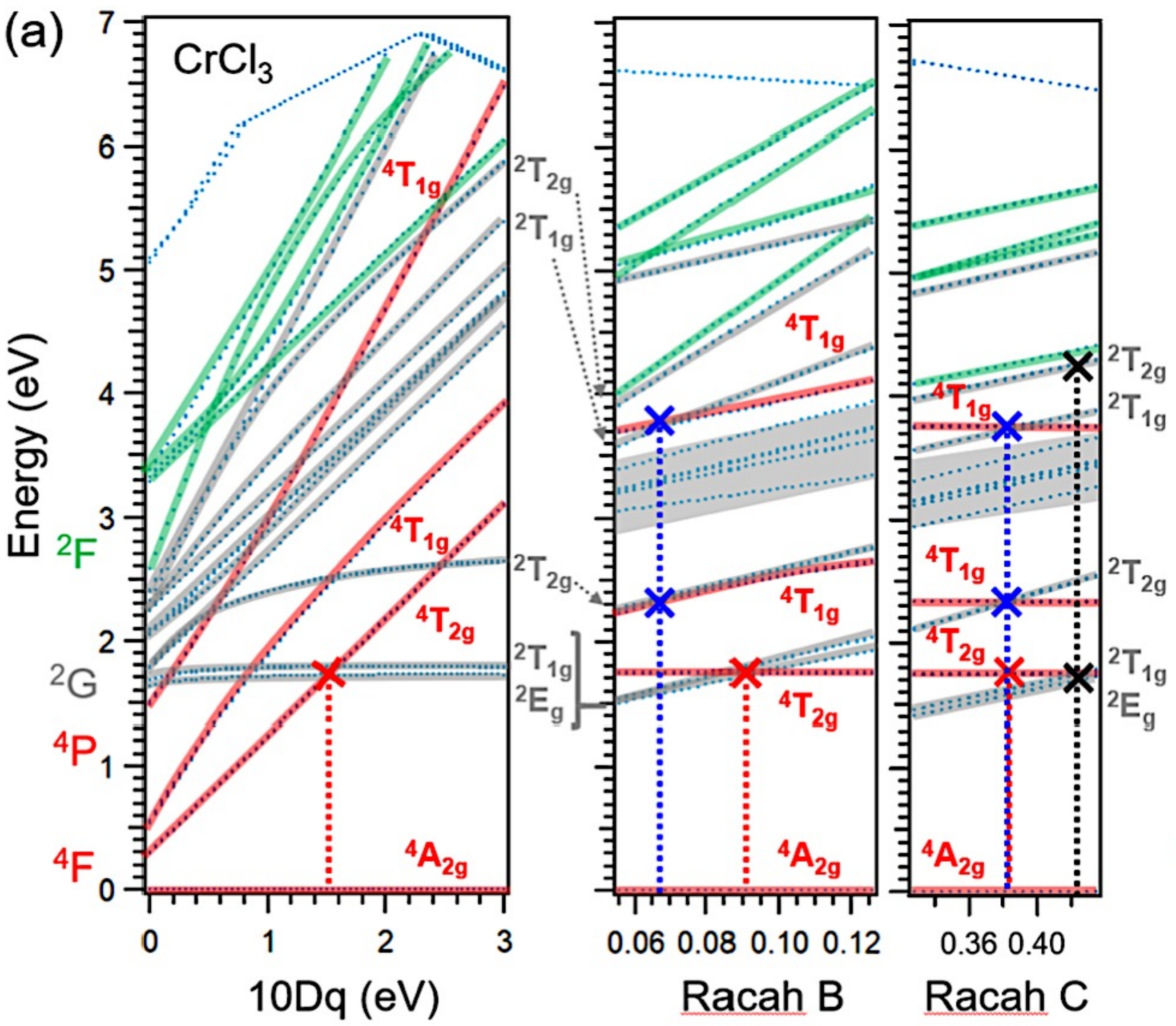
- Quanty use second quantization to define it's operators and the spectra are implemented by calculating the Green's function.

$$G(\omega) = \left\langle \psi_i \middle| T^\dagger \frac{1}{\omega - H + i\Gamma/2} T \middle| \psi_i \right\rangle$$

- In quanty simulation, the Hamiltonian and eigen states can be calculated for different parameters such as;
  - Atomic parameters ($U, F^0_{dd}, F^2_{dd}, F^4_{dd}, G^1_{pd}, G^3_{pd}, SOC$)
  - Crystal field parameters ($10Dq$)
  - LMCT parameters (Δ, V_{eg}, V_{t2g})
  - Magnetic field and exchange field etc



Calculating energy scales:



Energy scales …

➢ Racah Parameters (Interorbital coulomb interactions)

$$A = F_{dd}^{0} - \frac{F_{dd}^{4}}{9}$$

$$B = \frac{9 * F_{dd}^{2} - 5 * F_{dd}^{4}}{441}$$

$$C = \frac{5 * F_{dd}^{4}}{63}$$

➢ Interatomic exchange interaction

$$J_H = \frac{F_{dd}^{2} + F_{dd}^{4}}{14}$$

➢ Coulomb repulsion

$$U_{dd} = F_{dd}^{0} - \frac{2}{63}\left(F_{dd}^{2} + F_{dd}^{4}\right)$$

$$U_{pd} = F_{pd}^{0} - \frac{1}{15} G_{pd}^{1} - \frac{3}{70} G_{pd}^{3}$$

High resolution data analysis :

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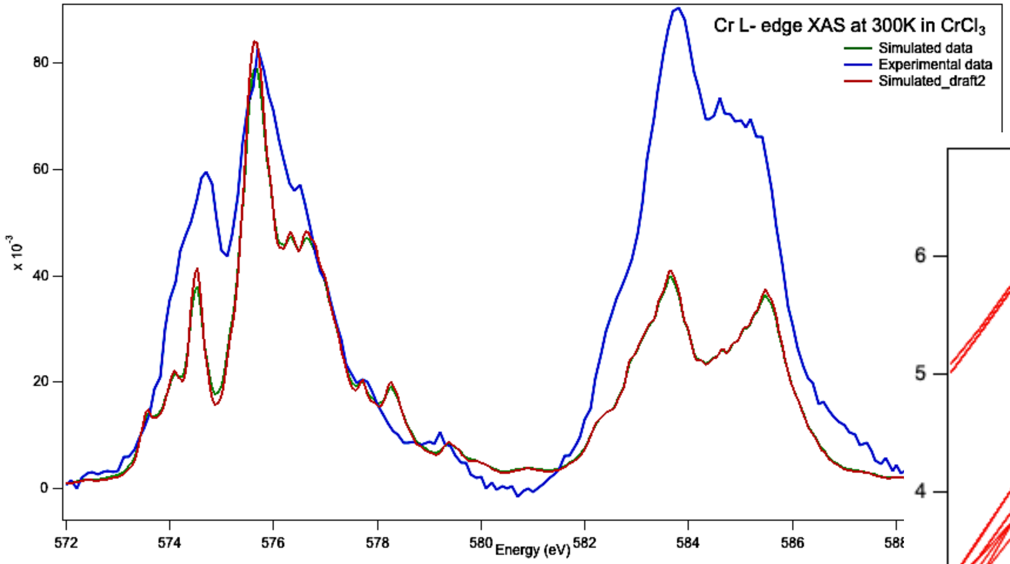
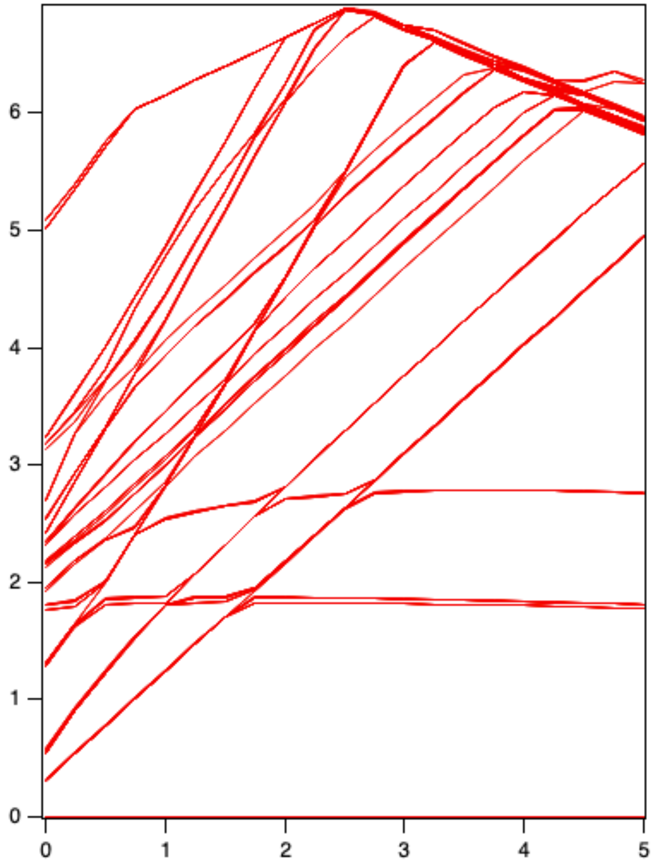
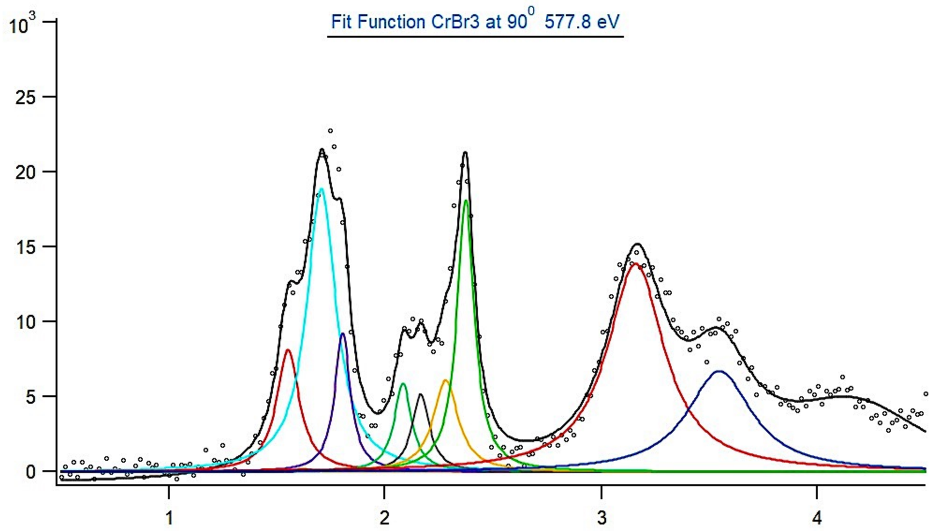






Conclusion :

- CrX_3 (X=Cl, Br and I) are becoming great potential candidates for spintronics and magnetoelectronic devices.
- RIXS is a much more accurate approach to obtain key energy scales than XAS and optical spectras.
- Using Quanty ELDs, we can reliably extract these energy scales and reconstruct RIXS spectra.

Acknowledgement :

Funding : NSF
Synchrotron radiation facilities :

ALS ADVANCED LIGHT SOURCE
HZB Helmholtz Zentrum Berlin
SPring-8
NSRRC

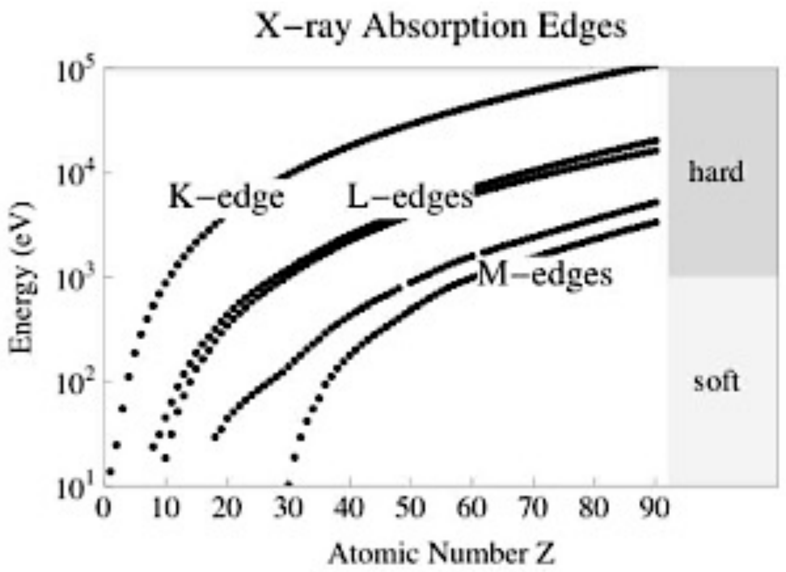
THANK YOU …

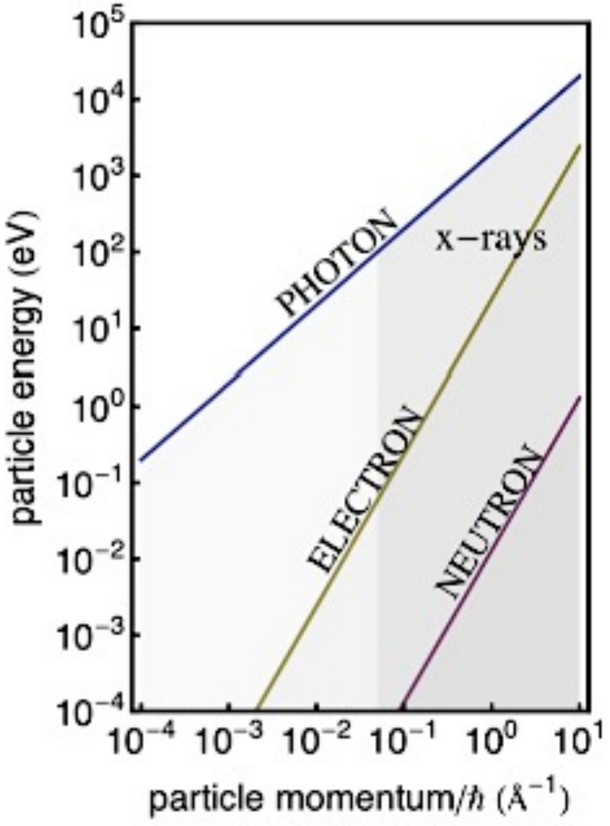
QUESTIONS ?

Why RIXS:

When comparing to other scattering techniques, RIXS has number of unique features.

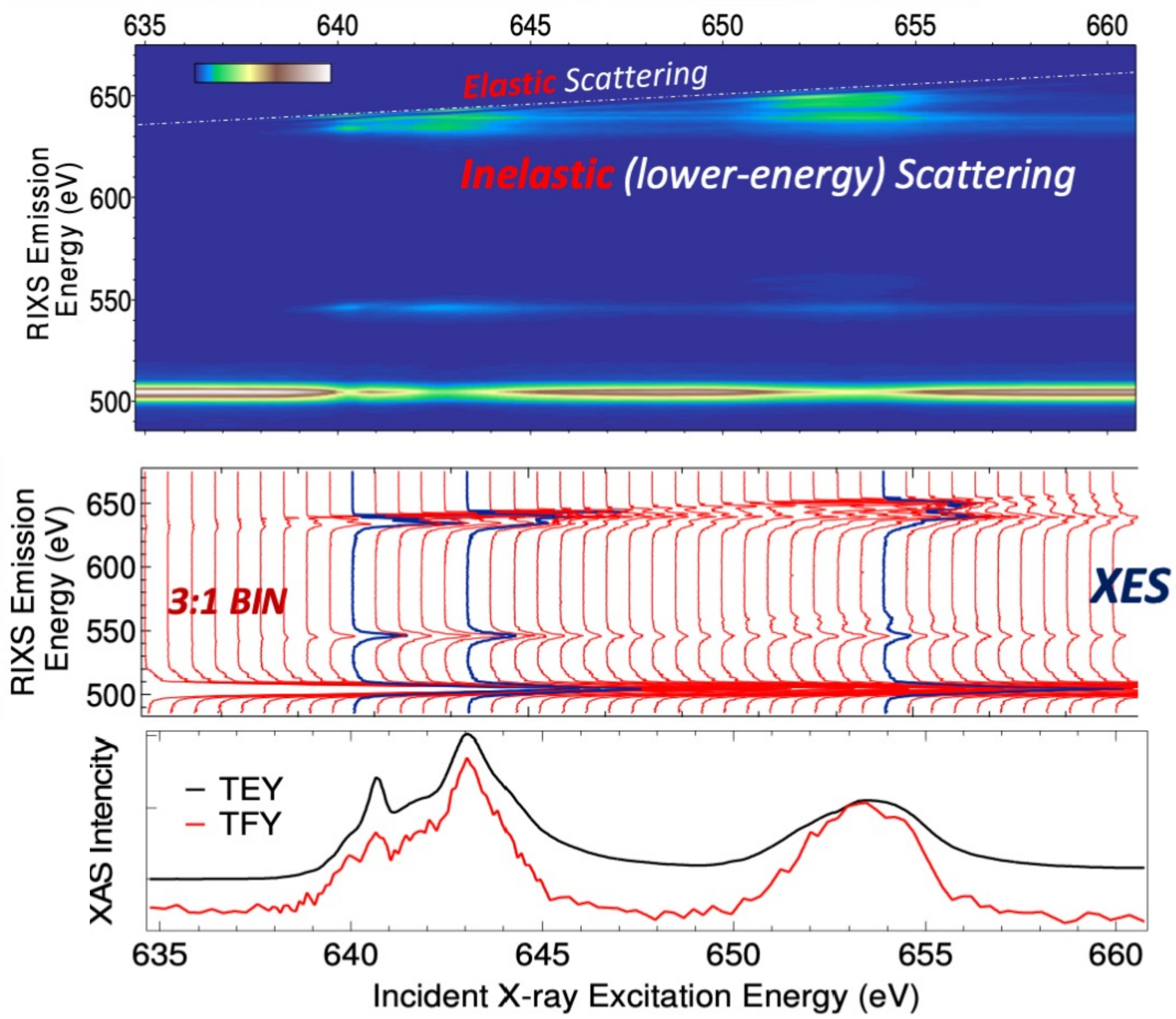
1. RIXS exploits both the energy and momentum dependence of the photon scattering cross-section.
2. RIXS can probe a very broad class of intrinsic excitations of the system under study
3. RIXS can utilize the polarization of the photon.
4. RIXS is element and orbital specific.
5. RIXS is bulk sensitive.
6. RIXS needs only small sample volumes.



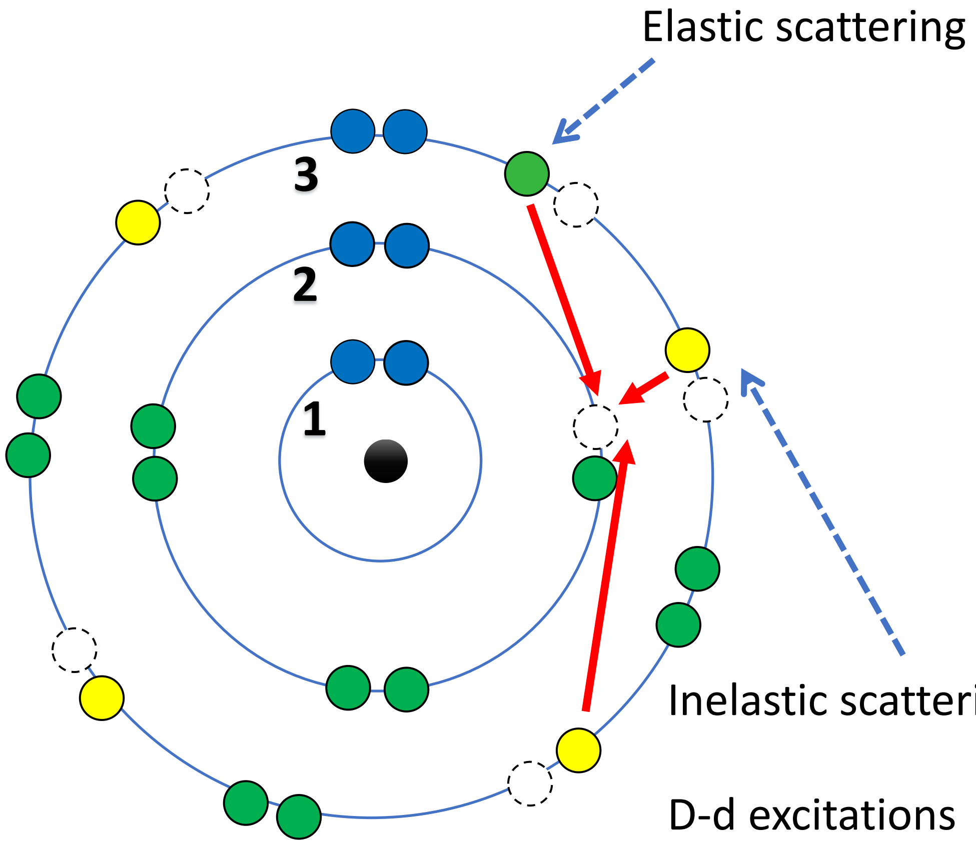


1. DOI: 10.1103/RevModPhys.83.705 · Source: arXiv

From XAS to Resonant Inelastic X-ray Scattering (RIXS) . . .



Detection :
Emitted photon.



D-d excitations
Charge transfer
Magnons
Phonons

Video : A "slow" explanation of XAS and RIXS through simplified Atomic Schematic

What is RIXS:

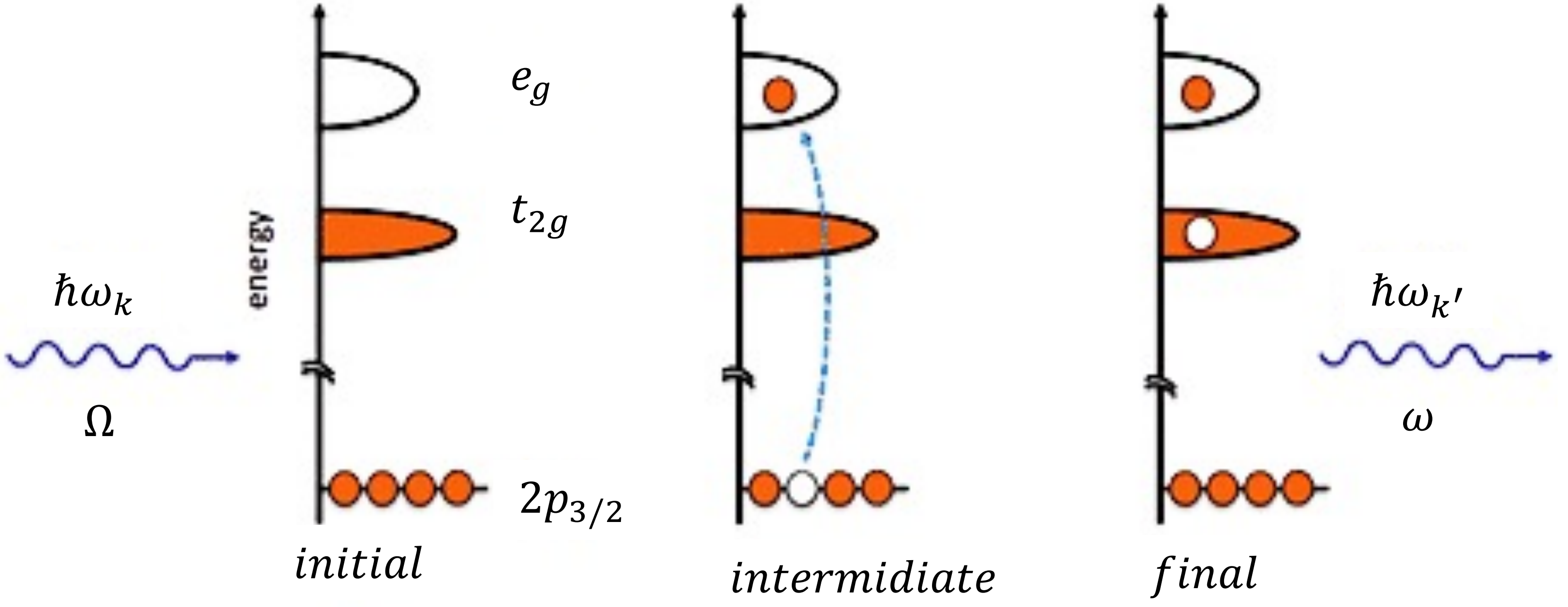
Kramers - Heisenberg cross section :

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left| < f|H_{int}|i> + \sum_{|n>} \frac{< f|H_{int}|n >< n|H_{int}|i >}{E_i + \hbar\omega_i - E_n + i\Gamma} \right|^2$$

ϵ - polarization
σ - cross section of the scattering
H_{int} describes interaction between photon and electrons
i, n and f - initial, intermediate and final states,
E_i , E_n , and E_f are the energies of the corresponding eigenstates,
Γ is the lifetime broadening of the intermediate state.

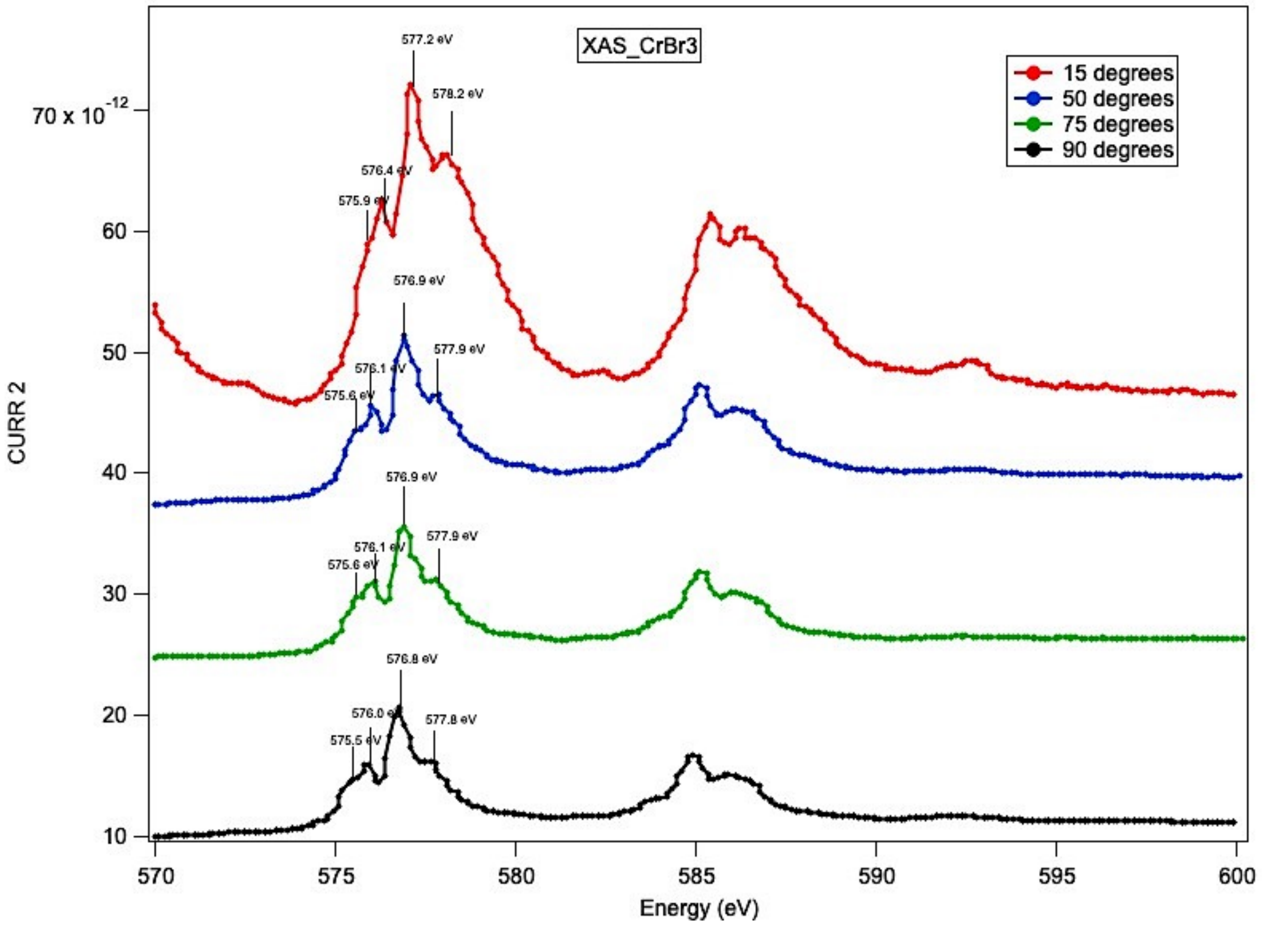
RIXS Intensity (scattering amplitude) :

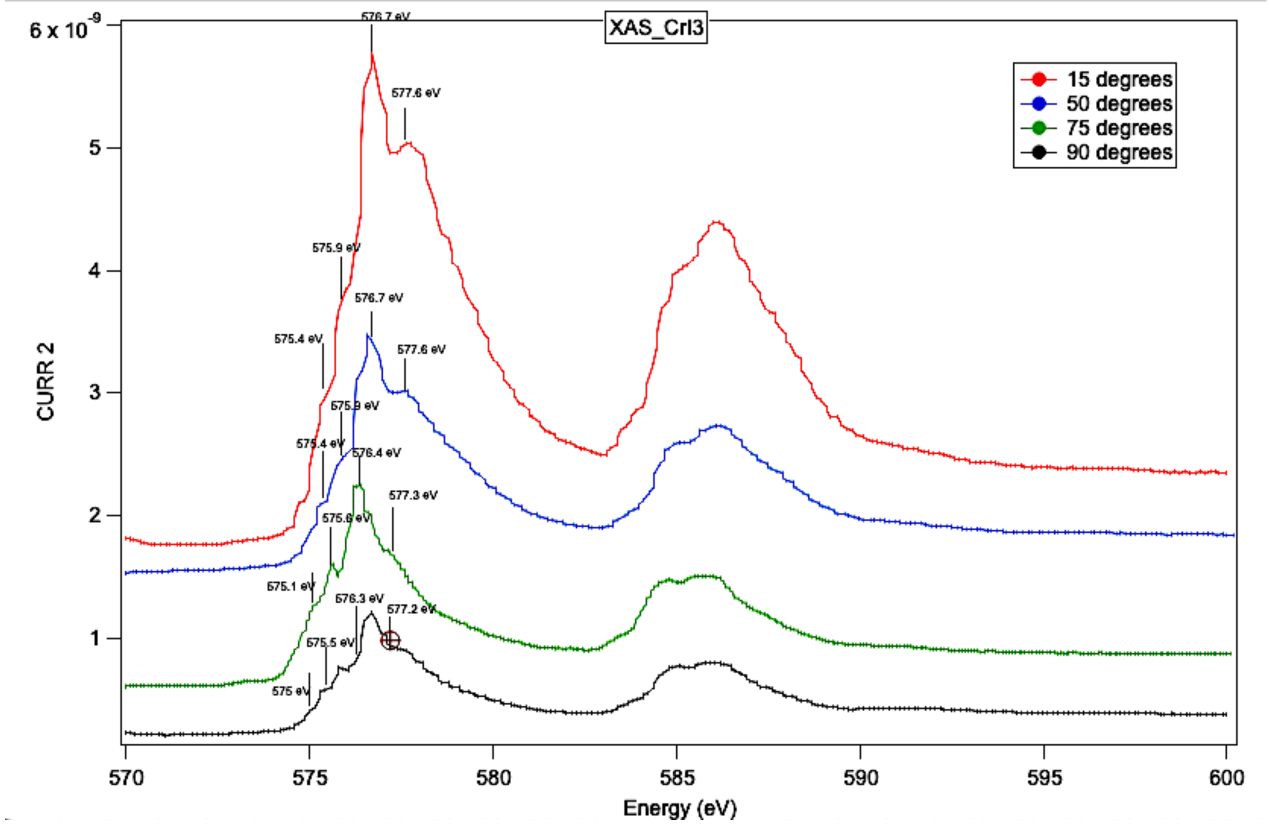
$$I(\omega, k, k', \epsilon, \epsilon') = \sum_f \left|\mathcal{F}_{fi}\,(\omega, k, k', \epsilon, \epsilon', \omega_k)\right|^2 * \delta(E_f + \hbar\omega_{k'} - E_i - \hbar\omega_k)$$



1. p. 2315-2366. Cham: Springer International Publishing, 2020.
2. RevModPhys.83.705 · Source: arXiv

Comparing X-ray Absorption Spectroscopy of CrX_3 (X = Cl, Br, I) :





RIXS studies of VI_3 VBr_3:

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- Two-Dimensional van der Waals material
- Ferromagnetic (FM) with $S = 1$
- Easily cleavable
- Curie temperatures Tc are higher than CrX_3 (80 and 98 K for VCl_3 and VI_3 monolayers, respectively).
- VI_3 is a Mott insulator which exhibits a SPT from monoclinic to rhombohedral at 79 K
- Long-range FM ordering appears at $Tc \approx 50$ K.

- Plan to perform series of RIXS measurements on VX_3 at the ALS qRIXS end station in order to obtain a comparison with the S=3/2 CrX_3 systems.
- We anticipate that RIXS will allow informative direct comparisons between Mott insulators and the metallic 2D magnets.
- Currently, we have the access to high quality VI_3 single crystals through the commercial laboratories.