Inelastic x-ray scattering, IXS

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Neutron and X-Ray Summer School
August 10-24, 2013
Argonne and Oak Ridge National Laboratory
• Nuclear Resonant Inelastic X-Ray scattering, NFS, NRIXS: Sectors 3, 16, (30)
• Momentum Resolved High Energy Resolution IXS (HERIX) Sectors 3, 30
• X-Ray Raman Scattering, XRS (LERIX): Sectors 13, 16, 20
• X-Ray Emission Spectroscopy, XES (MINIX): Sectors 13, 16, 17
• Resonant Inelastic X-Ray Scattering, RIXS (MERIX): Sectors 9, 30 --> 27
IXS: Inelastic X-Ray Scattering

A set of **vastly different** techniques based on measuring exact:

i) **energy**, and
ii) **momentum** transfer in a scattering experiment.

It provides **thermodynamic, elastic, electronic and chemical** information about the scattering system.

Since X-ray energies extend from a few eV to a few hundred keV, we need to measure energy loss or gain with a resolution changing from

- nano-eV
- meV,
- eV, and
- keV.
IXS: Inelastic X-Ray Scattering

IXS can measure
- nuclear hyperfine interactions (neV),
- collective excitations of atoms such as phonons (meV),
- electronic excitations like plasmons or magnons (eV),
- core-valence electron boundary to reconstruct the Fermi surface (keV)
- determine orbital occupancies (keV)

1920-1930: P. Debye, A. Compton and J. DuMond:

1960-1990: Development of
  i) pure silicon and germanium with $\Delta d/d \sim 10^{-9}$,
  ii) sophisticated high resolution monochromators, detectors
  iii) crystal analyzers and
  iv) the third generation synchrotrons

1990-present: More than a dozen new instruments around the world
6175 keV incident photons

Compton Scattered X-rays

Fluorescent X-rays

CeRh₃B₂

Elastic Peak

175 keV incident photons

Courtesy: Y. Sakurai, Spring-8
Inelastic X-Ray Scattering: A plethora of different techniques

### IXS

#### Non-Resonant

- ΔE ~ keV Compton

#### Resonant

- ΔE ~ meV IXS
- ΔE ~ 1 meV NRS
- ΔE ~ 100 meV RIXS

X-Ray Raman
X-Ray Emission
Inelastic X-Ray Scattering: A plethora of different techniques

- Non-Resonant
  - $\Delta E \sim \text{meV}$
  - IXS

- Resonant
  - $\Delta E \sim 1 \text{ meV}$
     - Nuclear resonant
Spatial variation
\( k = \text{wave number} \)
\( \lambda = \text{wavelength} \)

Temporal variation
\( \omega = \text{angular frequency} \)

Top view showing high and low field amplitudes
The incident plane wave incident upon an electron sets the electron in oscillation. The oscillating electron then radiates, experiencing a phase shift of $\pi$. 

Classical description of scattering of radiation by a charged particle.
First order Born approximation

For weakly scattering media, it is possible to obtain solution to the integral equation by a perturbation approach, provided that the scattering medium is weakly interaction with the probe of x-rays.

The first order Born approximation states that amplitude of the scattered wave far away from the scatterer depends entirely on one and only one Fourier component of the scattering potential, namely the one that corresponds to the transferred momentum $K=k(s-s_0)$. 

\[ p = \hbar k \]

\[ p' = \hbar k' \]

\[ q' = \hbar q' \]

\[ k' \]

\[ q' \]
Conservation of momentum has a correspondence between classical and quantum mechanical treatment:

\[ p = \hbar k \]

\[ \Delta p = p - p' = \hbar k' \]

If a plane wave is incident on the scatterer in the direction of \( s \), the Fourier component of the scattering potential can be determined.

And if one has the ability to vary the amount of momentum transfer at will, then, the scattering potential can be reconstructed.

This is the essence of x-ray scattering experiments.
What is being measured?

\[
\frac{d^2 \sigma}{d \Omega \, d \omega} = r_0^2 \frac{\omega_f}{\omega_i} \left| \mathbf{e}_i \cdot \mathbf{e}_f \right| N \sum_{i,f} \left| \langle i \left| \sum e^{i \mathbf{Q} \cdot \mathbf{r}_j} \right| f \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)
\]

Thomson cross section

\[ S(Q,\omega) = \frac{1}{2\pi} \int dt \ e^{-i \omega t} \left\langle \phi_i \left| \sum_{ll'} f_l(Q) e^{-i \mathbf{Q} \cdot \mathbf{r}_l(t)} f_{l'}(Q) e^{i \mathbf{Q} \cdot \mathbf{r}_{l'}(0)} \right| \phi_i \right\rangle \]

Dynamical structure factor \( S(Q,\omega) \)

Density-density correlations

\[ f(Q) = f_{ion}(Q) + f_{valence}(Q) \]

Atomic form factor
\[
S(Q, \omega) = \sum_{q,j} \sum_{s} f_s(Q) \frac{\hbar}{\sqrt{2m_s}} e^{-W_s} e^{i\vec{Q} \cdot \vec{R}_s} \left[ \bar{Q} \cdot \bar{e}(q,s,j) \right]^2 \left( \frac{1}{e^{\hbar\omega/kT} - 1} + \frac{1}{2} \pm \frac{1}{2} \right) \delta(\omega \pm \omega_{q,j})
\]
Atomic form-factor measurements in the low-momentum transfer region for Li, Be, and Al by inelastic x-ray scattering


\[ f(Q) = f_{\text{ion}}(Q) + f_{\text{valence}}(Q) \]

FIG. 2. Energy scans for lithium along the \([0 \zeta \zeta]\) direction for longitudinal modes.
The physical origin of the correlations depend on how $1/q$ compares with the characteristic length, $l_c$, of the system, which is related to spatial inhomogeneity (due to thermal or concentrations fluctuations)

when $q \cdot l_c \ll 1 \Rightarrow$ Collective excitations
when $q \cdot l_c \gg 1 \Rightarrow$ Single particle excitations
when $\frac{1}{q} \approx d$ and $\omega \approx$ phonon frequency $\Rightarrow$ Collective ion excitations (PHONON)
when $\frac{1}{q} \approx r_c$ and $\omega \approx$ plasma frequency $\Rightarrow$ Valence electron excitations
High-resolution inelastic x-ray scattering (IXS) at Sector 3 and Sector 30

IXS: Momentum resolved

High resolution monochromator

6 or 9 m horizontal arm

10 cm

1 mm

~11 cm

3 mm

mirror

HERIX-3

HERIX-30
30-ID-C: HERIX Spectrometer
Pressure fluctuations

\[ \omega_B(q) = V \cdot q \]

Entropy fluctuations,

\[ \Delta \omega_R \sim \alpha q^2 \]

Concentration fluctuations

\[ \Delta \omega_R \sim D q^2 \]

\[ \Delta \omega_B \sim V q^2 \]
High Energy Resolution Inelastic X-ray Scattering

APS-U will provide two enhanced HERIX spectrometers optimized for high-pressure and high-resolution work at HERIX-3-ID and HERIX-30-ID, respectively.

- High-pressure/high-temperature setup
  The goal: 2 Mbar, 2000 K

- 158 GPa
  cBN
  Fe
  100um

- Mineral physics and earth sciences
  Sound velocity, elastic constants

- Dynamics of liquids and liquid crystals stripe or nematic phases

- Role of phonons in pnictide superconductors
Phonons are periodic oscillations in condensed systems.

They are inherently involved in thermal and electrical conductivity.

They can show anomalous (non-linear) behavior near a phase transition.

They can carry sound (acoustic modes) or couple to electromagnetic radiation or neutrons (acoustical and optical).

Have energy of ħω as quanta of excitation of the lattice vibration mode of angular frequency ω. Since momentum, ħk, is exact, they are delocalized, collective excitations.

Phonons are bosons, and they are not conserved. They can be created or annihilated during interactions with neutrons or photons.

They can be detected by Brillouin scattering (acoustic), Raman scattering, FTIR (optical).

Their dispersion throughout the BZ can ONLY be monitored with x-rays (IXS), or neutrons (INS).

Accurate prediction of phonon dispersion require correct knowledge about the force constants: COMPUTATIONAL TECHNIQUES ARE ESSENTIAL.
Dispersion relations and phonon density of states
\( \alpha \) -iron (bcc)

V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. 162 (1967) 528, and
Dispersion relations

\[ \omega(k) = 2\omega(\sin|ka/2|) \]

\[ \frac{\partial \omega_k}{\partial k} : \text{sound velocity} \]
\[ E = \frac{2\hbar}{\pi} V_L Q_{\text{max}} \sin \left( \frac{\pi}{2} \frac{Q}{Q_{\text{max}}} \right) \]

\[ E(\text{meV}) = 4.192 \cdot 10^{-4} \cdot V_L (\text{m/sec}) Q_{\text{max}} \left( \text{nm}^{-1} \right) \cdot \sin \left( \frac{\pi}{2} \frac{Q}{Q_{\text{max}}} \right) \]

\[ V_L = \sim 5000 \text{ m/sec} \]

\[ P > 1 \text{ atm} \]
Why x-rays instead of neutrons or visible light?

Limited momentum transfer capability of neutrons at low energies favor x-rays to study collective excitations with large dispersion, like sound modes.

When the sound velocity exceeds that of neutrons in the liquid, x-rays become unique. The low-momentum/high-energy transfer region is only accessible by x-rays.
Why X-Rays?

Neutrons X-rays

Lindemann criterion: \( m v_{\text{sound}}^2 \propto T_{\text{melt}} \)

Melting point (K)

Sound velocity (m/s)

- Neutrons
- X-rays
- Laser heating

Pressure fluctuations:
- \( \Delta \omega_B \sim Vq^2 \)
- \( \omega_B(q) = V \cdot q \)

Entropy fluctuations, Concentration fluctuations
- \( \Delta \omega_R \sim \alpha q^2 \)
- \( \Delta \omega_R \sim D q^2 \)

Nuclear resonant-elastic Scattering

Nuclear resonant-inelastic Scattering

Electrons

Neutrons

Light

Rayleigh

Brillouin

\( \Delta E \)

\( V_{\text{x-ray}} \)

\( V_{\text{liquid}} \)

\( V_{\text{neutron}} \)

\( \Delta p \)

Thermal neutrons

Laser heating

\( \Delta \omega_B \sim Vq^2 \)

\( \omega_B(q) = V \cdot q \)
Methodology developments

Cryo-cooled monochromators

$^{119}\text{Sn} @ 14.4 \text{ keV}$
$\partial E = 1.3 \text{ meV}$

$^{151}\text{Eu} @ 21.5 \text{ keV}$
$\partial E = 1.4 \text{ meV}$

Thomas Toellner, Deming Shu, APS
Acoustic phonons in chrysotile asbestos, Mg₃Si₂O₅(OH)₄

Damped harmonic oscillator model

Longitudinal sound velocity

\[ S(h\omega) = \frac{1}{1 - e^{-\hbar\omega/kT}} \left[ I_c \frac{1}{\pi} (\hbar\omega)^2 + I_Q \frac{4\Gamma_Q(h\omega_Q)(h\omega)}{\pi} \right] \]

\[ \Omega_Q = \left( (\hbar\omega_Q)^2 + \Gamma_Q^2 \right)^{1/2} \]

\[ E = \frac{2V_L\hbar Q_{\text{max}}}{\pi} \sin \left( \frac{\pi Q}{2 Q_{\text{max}}} \right) \]

\[ E (\text{meV}) = 4.192 \cdot 10^4 V_L Q_{\text{max}} \sin \left( \frac{\pi Q}{2 Q_{\text{max}}} \right) \]

**Pnictides: A scientific opportunity for IXS:**

![Diagram of Pnictide Structures](image)

- **Pnictogen:** P, As
- **Chalcogen:** S, Se, Te

Are pnictides BCS type electron-phonon superconductors? Is Migdal-Eliashberg theory obeyed?

\[
\ln \frac{\lambda}{2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
\]

\[
1 - \frac{1.04(1 + \lambda)(1 + 0.62\lambda)\mu^*}{[\lambda - \mu^*(1 + 0.62\lambda)]^2},
\]

\[
1 + 12.5 \left( \frac{T_c}{\omega_{\ln}} \right)^2 \ln \left( \frac{\omega_{\ln}}{2T_c} \right),
\]

\[
\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega/\omega
\]

electron-phonon coupling constant

\[
\ln \omega_{\ln} = (2 / \lambda) \int \ln \omega \alpha^2 F(\omega) \frac{d\omega}{\omega}
\]
is the relevant phonon frequency

For pnictides values of \( \lambda \) is inconsistent with observed \( T_c \). Estimated value of 0.2 is too small for the observed 26 K transition temperature.

~ 26 K, SC transition temperature
Isotope effect coefficient
SC energy gap / \( T_c \) ratio

\( \ln \omega_{\ln} \) is close to the values obtained above.
LaFeAsO$_{1-x}$F$_x$

\[
\lambda_{\nu q} \equiv \frac{1}{\pi N(0)} \frac{\gamma_{\nu q}}{\omega_{\nu q}^2}
\]

Oxygen modes do not contribute much to Eliashberg function

NRIXS: Element selective partial phonon dos

Electron-phonon linewidth
Influence of magnetism on phonons in CaFe$_2$As$_2$ as seen via inelastic x-ray scattering

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CaFe$_2$As$_2$ under pressure

There is a phase transition from magnetically ordered orthorhombic phase to a nonmagnetic “collapsed” tetragonal phase, accompanied by a significant volume change at 0.3 GPa.
In the experimental measurements were compared to study the dispersion and potential line broadenings.

The relation between the Miller indices in the tetragonal $Pbnm$ phase are, in spin-Polarized Perturbation Theory ($SPPT$) calculations, also in spin-Polarized calculations.

FIG. 8
Compared to nonmagnetic calculations, this might explain why the position of the $Q = (0.0,0.8)$ feature is x$q$ times stronger in better agreement with those of Ref. \[1,2\], where a small change in the experimental lattice parameters at room temperature in the tetragonal phase.

The relation (elongation or shrinking) of the Fe-As tetrahedra sheets have a dominant effect of the magnetization on Fe is to strongly split these states.

Also, we checked by calculations in the virtual spin-down states, and the results are in very good agreement with those of Ref. \[1,2\].

The acoustic mode is slightly softer and has greater intensity. The upper $LaAs$ mode is essentially created by the energy to improve visibility of the optical modest. The ratio of intensities between the acoustic and optical modes.

Figure 8

The acoustic mode is slightly softened in better agreement with those of Ref. \[1,2\].

The acoustic mode is slightly softer and has greater intensity. The upper $LaAs$ mode is essentially created by the energy to improve visibility of the optical modest. The ratio of intensities between the acoustic and optical modes.

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**BaFe_{1.8}Co_{0.2}As_{2}**


Non-magnetic calculations vs experiment

Magnetic calculations vs experiment

Comparison of measured and calculated phonon frequencies with experiment upon inclusion of magnetism speaks in favor of large antiferromagnetic Fe moments. The destruction of the magnetic order by either doping or conductivity appears to only weakly, if at all, influence the high-energy modes upon doping. We also found that superconductivity appears to only weakly, if at all, influence the high-energy modes upon doping.
Sound velocity at the conditions of the Earth’s core in iron alloys
Direct measurements of the $V_p$ relationship of Fe-light element alloys at relevant P-T conditions of the core now appear to be on the horizon, which in turn may eventually answer the longstanding question on the composition of the Earth’s core.
Sound velocity at the conditions of the Earth’s core in iron alloys

![Graph showing sound velocity vs. pressure for different Fe alloys at the Earth's core conditions.](image)

**Legend:**
- **HERIX**
- **NRIXS**
- **ISLS**
- **OC** (outer core)
- **IC** (inner core)
- **hcp-Fe**

**Note:** ISLS: impulsive stimulated light scattering
Dispersion relations and phonon density of states

$\alpha$ -iron (bcc)

Fig. 4.

Displacement relations

\[ \omega(k) = 2\omega(\sin|ka/2|) \]

\[ \frac{\partial \omega}{\partial k} : \text{sound velocity} \]
\[E = \frac{2\hbar}{\pi} V_L Q_{\text{max}} \sin\left(\frac{\pi}{2} \frac{Q}{Q_{\text{max}}}\right)\]

\[E(\text{meV}) = 4.192 \cdot 10^{-4} \cdot V_L (\text{m/sec}) Q_{\text{max}} (\text{nm}^{-1}) \cdot \sin\left(\frac{\pi}{2} \frac{Q}{Q_{\text{max}}}\right)\]
a few questions

- Can one measure phonon dispersion and/or phonon dos
  - from a monolayer?
  - at a buried interface?
  - from nanosized particles on the surface?
  - at 3 Mbar and at 4 K to 5000K extreme conditions?
  - from a nanogram sample?
  - in a way that is element and isotope selective?
  - in a way that can be completely tested by DFT, i.e. both the frequency and amplitude of vibrations are determined
Characteristics of a Mössbauer nuclei

$^{57}$Co

$t_{1/2} = 270$ days

Electron capture

$^{57}$Fe

$t_{1/2} = 8.7$ ns, $\Gamma = 52$ neV

$t_{1/2} = 97.8$ ns, $\Gamma = 4.6$ neV

$t_{1/2} = \infty$, $\Gamma = 0$

Transitions to ground state with a relatively low energy is what makes a nuclei a Mössbauer nuclei
Nuclear Resonance and Fallout in $^{57}$Fe-decay

- Conversion electrons, Auger electrons
- K fluorescence induced by nuclear decay
- 14.413 incoherent nuclear fluorescence
- 14.413 coherent nuclear fluorescence
- Photoelectrons, Auger electrons
- K fluorescence
- 14.413 Rayleigh photons
- Compton scattered photons

14.413 keV
Standard Time structure @ APS

1 revolution = 3.68 µsec => 1296 buckets

60% of the time @ the APS

153 nsec
Detection of nuclear decay

**Prompt Photons**

- **Energy**: 136 keV
- **Spin, I**: 5/2, 3/2, 1/2
- **Decay**: 9% 91%

**Delayed Photons**

- **Energy**: 14.41256 keV
- **Spin, I**: 5/2, 3/2, 1/2
- **Decay**: 9%

**Exponential Decay**
Detailed Balance

\[ I(-E) = I(E)e^{-E/kT} \]

\[ T = \frac{E(eV)}{k_B \ln[I(E)/I(-E)]]} \]

\((-22.6\,\text{meV}, 1158)\)

\((22.6\,\text{meV}, 2762)\)

phonon annihilation

phonon creation

1-phonon

2-phonon

3-phonon

Energy (meV) \( (E_0=14.41256\,\text{keV}) \)
$I(-E) = I(E)e^{-E/kT}$

$k_B = 8.6173 \cdot 10^{-2} \text{ meV} / K$

$E = 22.6 \text{ meV}$

$I(-E) = 1158$, $I(E) = 2762$

$T = \frac{E(eV)}{k_B \ln[I(E)/I(-E)]} = 297.03K$

Energy (meV) ($E_0=14.41256 \text{ keV}$)
How to measure temperature in a DAC?

\[ I(E) = I(-E) e^{(E/kT)} \]

\[ \int I(E) dE = \int I(-E) e^{(E/kT)} dE \]

Temperature dependence of phonon excitation probability

Figure 6. Energy spectra of inelastic nuclear absorption of synchrotron radiation by $^{57}$Fe at various temperatures. Solid lines are calculations according to eqs. (5.1)–(5.3), based on the results of neutron scattering at room temperature [15] and convoluted with the instrumental function of the monochromator. From [14].

At low temperatures, besides vanishing in the phonon-annihilation part, the energy spectrum of inelastic absorption also vanishes at the low energy transfer region in the Chumakov, et al, Phys. Rev. B 54 (1996) 9596.
Lipkin’s sum rules related to phonon excitation probability

\[ \langle E_1^1 \rangle = E_R = \frac{E_\gamma^2}{2Mc^2} \]

Recoil energy

\[ \langle E_2^2 \rangle = 4E_R \bar{T} \]

Kinetic energy

\[ \langle E_3^3 \rangle = \left( \frac{2\hbar^2 E_R}{M} \right) \frac{\partial^2 U}{\partial z^2} \]

Force constant

\[ E_R = \frac{(\hbar k)^2}{2M} = 1.96 \text{ meV} \]

Extraction of phonon density of states

\[ D(E) = \frac{3E}{E_R} \frac{S'(E)}{f} \left[ 1 - e^{-E/kT} \right] \]
Expression 1:
\[ g(E) = \sum_s \frac{dN_s}{dE} = \frac{VE^2}{h^3} \sum_s \int \frac{1}{v_s^3} d\Omega_q \]

Expression 2:
\[ \frac{1}{v_D^3} = \frac{1}{3} \sum_s \int \frac{1}{v_s^3} \frac{d\Omega_q}{4\pi} \]
Measurement of $v_D$, Debye sound velocity allows to resolve longitudinal and shear sound velocity, provided that bulk modulus and density, is independently and simultaneously measured by x-ray diffraction.

\[ g(E) = \frac{\tilde{m}}{2\pi^2 \hbar^3 \rho v_D^3} E^2 \]

\[ \frac{K_S}{\rho} = V_P^2 - \frac{4}{3} V_S^2 \]

\[ \frac{G}{\rho} = V_S^2 \]

\[ \frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3} \]

**$K_S$**: adiabatic bulk modulus  
**$G$**: shear modulus  
**$V_P$**: compression wave velocity  
**$V_S$**: shear wave velocity  
**$V_D$**: Debye sound velocity  
**$\rho$**: density
Phonon density of states of iron under high pressure

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<thead>
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<th>Property</th>
<th>Information content</th>
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| Lamb-Mössbauer Factor, or recoil-free fraction                          | \( f_{LM} \), recoil free fraction obtained from density of states. \( g(E) \):  
\[
f_{LM} = \exp \left( -E_R \int \frac{g(E)}{E} \cdot \coth \frac{\beta E}{2} dE \right)
\]                                                                                                         |
| Second order Doppler shift                                              | \( \delta_{SOD} = -E_0 \frac{v^2}{2c^2} \)                                                                                                                                                                         |
| Average kinetic energy                                                 | Extracted from second moment of energy spectrum:  
\[
T = \frac{1}{4E_R} \left\langle \left( E - E_R \right)^2 \right\rangle
\]                                                                                                         |
| Average force constant                                                 | Extracted from third moment of energy spectrum:  
\[
\frac{\partial^2 U}{\partial z^2} = \frac{m}{2\hbar^2} \left\langle E^3 \right\rangle
\]                                                                                                         |
| Phonon density of states                                               | Extracted one-phonon absorption probability, \( S_1(E) \):  
\[
g(E) = \frac{E}{E_R} \tanh \left( \frac{\beta E}{2} \right) \left( S_1(E) + S_1(-E) \right)
\]                                                                                                         |
| Specific heat (vibrational part only)                                  | \( C_V = 3k_B \int_0^{\infty} \left\langle \frac{\beta E}{2} \right\rangle^2 \csc h(\beta E) \ g(E) \ dE \)                                                                                                      |
| Vibrational entropy                                                    | \( S_V = 3k_B \int_0^{\infty} \left[ \frac{\beta E}{2} \coth(\beta E) - \ln \left( 2\sinh(\beta E) \right) \right] g(E) \ dE \)                                                                          |
| Debye sound velocity (aggregate sound velocity)                        | From low-energy portion of the density of states:  
\[
g(E) = \frac{3V}{2\pi^3 V_D^3} E^2
\]                                                                                                         |
| Mode specific vibrational amplitude                                    | Contribution of mode \( \alpha \) of atom \( j \) to zero-point fluctuation [11,12]:  
\[
\left\langle r_{j\alpha}^2 \right\rangle_0 = \frac{\hbar^2}{2m_j \omega_\alpha^2} e_{j\alpha}^2
\]                                                                                                         |
| Mode specific Gruneisen constant                                       | From pressure dependence of phonon frequencies \( \omega_\alpha \) of acoustic or optical modes:  
\[
\gamma_\alpha = -\frac{\partial \ln \omega_\alpha}{\partial \ln V}
\]                                                                                                         |
| Temperature of the sample                                              | From detailed balance between phonon occupation probability                                                                                                                                            |
Some unique advantages of NRIXS

1. Low frequency motions: ~ total mass
2. No selection rule except motion of atoms along x-ray propagation
3. Peak intensity ~ mode participation ~ actual displacement
4. No matrix effects or limitations
5. Element and isotope selective
6. No unpredictable cancellations in scattering terms

\[ \phi_\alpha = \frac{1}{3} \frac{\overline{V}_R}{\overline{V}_\alpha} e^{2} j_\alpha (\overline{n}_\alpha + 1) f \]

**Porphyrs:**

**Tetraphenylporphyrin (TPP)**

**Octaethylporphyrin (OEP)**

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<tr>
<th>A</th>
<th>B</th>
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<tbody>
<tr>
<td>Phenyl</td>
<td>H</td>
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<td>H</td>
<td>Ethyl</td>
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