

*auntie*CLIMAX*

a users guide to Version 3.0

distributed with version 4.0

by

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CLIMAX is the name of a program that calculates the INS spectrum of isolated molecules within the Bright-Wilson formalism. It is the best of its kind and a yardstick by which others are found wanting.

aCLIMAX, takes a different approach but aims to be of equal standing in the community.

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Overview

aCLIMAX [1] is an unsupported stand alone program running in Visual Basic. It is used to interpret inelastic neutron scattering (INS) spectra taken on TOSCA like spectrometers; i.e. spectrometers with very good energy resolution operating over broad energy transfer ranges with low final energies.

Correctly assigned INS spectra of simple model compounds are invaluable in understanding the spectra of more complex systems. As an example; the assigned spectra of several model compounds could act as a source of vibrational motifs for comparison with, say the INS results obtained from a hydrocarbon adsorbed on a catalytic surface. Achieving a convincing assignment for model compounds is, therefore, a matter of great importance. aCLIMAX supports the use of *ab-initio* calculations as tools to provide the best assignment schemes for their observed INS spectra. The calculations presented here are based on those used in the CLIMAX program that, despite its limitations, has been successfully used to fit *ab-initio* results to INS data [2].

Two general types of forces control the overall shape of an INS spectrum and in the limit of ideality they can be separated. The first comes from the internal field, which allows molecular identity to be maintained in the gas phase and is responsible for internal dynamics (ideally relative atomic displacements without motion of the centre of molecular mass). The second comes from the external field, which maintains the molecular crystal as a solid and governs the external, or lattice, dynamics (ideally displacements of the centre of molecular mass without relative motions of the atoms within a given molecule). This idealistic separation of forces is surprisingly successful but it must not be imagined that it is globally valid, specific intermolecular interactions, like hydrogen bonds, are not subject to this approach.

We can exploit this approximation and use *ab-initio* programs working on single molecules to calculate the motion of the atoms in the internal vibrational modes and subsequently use approximate shapes to represent the external modes. Programs, like GAUSSIAN '98 and DMOL [3] are fast, accurate, widely supported and simple to use. They are easily capable of producing all the raw data needed to produce the INS spectrum for many organic molecules. Moreover, these programs are familiar to the wider chemical community

Here we present a convenient method of generating the INS spectrum from such *ab-initio* results, aCLIMAX. This program follows current best practices and incorporates harmonic events beyond the two-quantum level, as well as anisotropic external Deby-Waller effects. The theory of INS spectroscopy will be introduced in terms of the mathematical framework used in aCLIMAX and all of the working equations are derived or referenced. The necessary computing environment and software packages are detailed. The description of aCLIMAX is given in terms of its required inputs. Working within the frame of known approximate methods the external displacements of molecules is outlined. Our conceptual approach to the calculated spectrum and its relationship to the observed INS spectrum is presented. Finally worked examples demonstrate how the package works. Some supporting software is presented.

1. Inside the Black-Box

1.1 Introduction to Scattering Theory

The fundamental theory of INS spectroscopy was developed very soon after the first nuclear piles began operating and is well covered in standard texts [4].

When analysing the results of a neutron experiment we shall need to relate the number of neutrons seen in our detector as it is positioned at different angles around the sample. If the detector subtends a small solid angle, $d\Omega$, at the sample the differential cross section is

$$\frac{d}{d\Omega} \cdot \sigma = \frac{\text{number of neutrons seen by the detector (per second)}}{\text{number of incident neutrons (per second)}} \cdot \frac{1}{d\Omega}$$

The flux of a beam of particles is the product of their velocity and density, $v \cdot \rho$. The required density is $\rho = |\psi|^2$

The incident wave function is plane wave in nature and the scattered wave is spherical in nature, see below, and are conveniently written

$$\psi_i = \exp(i \frac{2\pi}{\lambda_i} \cdot \mathbf{r}), \quad |\psi_i|^2 = 1 \quad \psi_f = \frac{\beta}{|\mathbf{r}|} \exp(i \frac{2\pi}{\lambda_f} \cdot \mathbf{r}), \quad |\psi_f|^2 = \left(\frac{\beta}{r}\right)^2$$

If the detector is a distance, r , away from the sample and has an area, ds , then $d\Omega = ds/r^2$. In elastic scattering the incident and final velocities are equal.

$$\frac{d\sigma}{d\Omega} = \beta^2 \cdot \frac{v_f}{v_i} \cdot \frac{ds}{r^2} \cdot \frac{1}{d\Omega} = \beta^2$$

$$\int_{4\pi} \frac{d\sigma}{d\Omega} = \int_{4\pi} \beta^2 = \sigma, \quad \therefore \beta^2 = b^2$$

If the neutron exchanged energy with the scattering system the differential scattering cross section must contain energy terms.

$$\frac{d^2\sigma}{dE \cdot d\Omega} = \frac{v_f}{v_i} \cdot \left(\frac{m}{2\pi\hbar^2}\right)^2 \cdot \left| \langle \psi_f \Psi_f | V(\mathbf{r}) | \psi_i \Psi_i \rangle \right|^2 \cdot \delta(E_i - E_f + \hbar\omega)$$

There are four terms in the expression the first is the ratio of the incident and final neutron velocities. The second term groups the fundamental constants and the final term ensures that the total energy of the system is conserved; ie that the difference between the incident and final neutron energies, E , equals a quantised energy state of the system, $\hbar\omega$; or zero for elastic scattering. The third term describes how the initial states are related to the final states through the scattering potential, $V(\mathbf{r})$. (Where Ψ is the wave function of the scattering system.) This expression is valid only if the perturbation introduced by the presence of the scatterer is weak. This is not strictly true since it is known that neutrons are scattered by the ‘strong nuclear force’. However this force is extremely short ranged and may therefore be successfully

approximated, the Born approximation, to a weak perturbation. Only one form for $V(\mathbf{r})$ can successfully reproduce spherical (S-) wave scattering from nuclei, the Fermi pseudo-potential, arising from a series of atoms l at positions \mathbf{R}_l .

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \cdot \sum_l b_l \cdot \delta(\mathbf{r} - \mathbf{R}_l)$$

P-waves are not observed in neutron scattering experiments, because the neutron energies are too low. The P-wave has little amplitude at the small radial values typical of atomic nuclei. (This will be familiar to chemists in the shape of electron p-orbitals in atoms.) It is clear then that the basis of neutron scattering rests on a series of approximations that are good only because the neutron interacts weakly, ie infrequently, with samples. Moreover, the strength of these interactions, expressed as b , are experimentally determined observables with, as yet, no simple theoretical basis.

It is convenient rewrite the double differential scattering crosssection equation in terms of a van Hove response function, S , which emphasises the structure and dynamics of the sample, the 'Scattering Law'.

$$S(\mathbf{Q}, \omega) = \frac{4\pi}{\sigma} \cdot \frac{\mathbf{k}_i}{\mathbf{k}_f} \cdot \left(\frac{d^2\sigma}{dE \cdot d\Omega} \right)$$

where

$$\mathbf{k}_{i(f)} = \frac{2\pi}{\lambda_{i(f)}} \quad ; \quad \mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \quad \quad Q = |\mathbf{Q}|$$

The response function is

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar} \cdot \int_{-\infty}^{\infty} dt \cdot \exp(-i\omega t) \cdot \sum_l Y_l(\mathbf{Q}, t)$$

and the correlation function, Y , gives the evolution of the scattering system in time, t .

1.2 Inelastic Scattering

The correlation function

$$Y(\mathbf{Q}, t) = \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}(0)) \cdot \exp(i\mathbf{Q} \cdot \mathbf{R}(t)) \rangle$$

represents the position, $\mathbf{R}(t)$, of an atom of, say, hydrogen at time, t , if it was originally at $\mathbf{R}(0)$ at $t = 0$. It is conventional to decompose the atomic position into vectors within a molecular framework, $\mathbf{R}(t) = \mathbf{c}(t) + \mathbf{I}(t) + \mathbf{u}(t)$. Where the position of the molecular centre of mass is given by the vector, $\mathbf{c}(t)$. The internal vector, $\mathbf{I}(t)$, determines the mean atomic position w.r.t the centre of mass and $\mathbf{u}(t)$ its vibrational displacement. This leads to expressions similar to the general correlation function, with that for vibration being

$$Y(\mathbf{Q}, t)_{\text{vib}} = \langle \exp(-i\mathbf{Q} \cdot \mathbf{u}(0)) \cdot \exp(i\mathbf{Q} \cdot \mathbf{u}(t)) \rangle$$

Where the scattering law has been decomposed according to the separation of forces

$$S_{\text{Total}} = S_{\text{Translation}} \otimes S_{\text{Rotation}} \otimes S_{\text{Vibration}}$$

Using $\langle \exp A \cdot \exp B \rangle = \exp \langle A^2 \rangle \cdot \exp \langle A \cdot B \rangle$. We can rewrite, for example, S_{vib} .

$$S(\mathbf{Q}, \omega)_{\text{vib}} = \int_{-\infty}^{\infty} dt \cdot \exp(-i\omega t) \underbrace{\exp(-i\mathbf{Q}^2 \cdot \langle U(0)^2 \rangle)}_{\text{time independent}} \underbrace{\exp(i\mathbf{Q}^2 \cdot \langle U(0) \cdot U(t) \rangle)}_{\text{time dependent}}$$

Performing the Fourier transform from the time to the frequency domain it can be appreciated that the time independent terms will include contributions from all frequencies whilst time dependent terms will be specific to particular frequencies. The form for a simple harmonic oscillator at frequency ω , is:

$$S(\mathbf{Q}, n\omega)_{\text{vib}} = \exp(n\Theta) \cdot \exp(-\Phi) \cdot \mathbf{I}_n(\Lambda) \quad (1)$$

$$\Theta = \frac{\hbar\omega}{2k_B T}; \quad \Phi = \mathbf{Q}^2 \cdot \frac{\hbar}{2\mu\omega} \cdot \text{coth}(\Theta); \quad \Lambda = \mathbf{Q}^2 \cdot \frac{\hbar}{2\mu\omega} \cdot \text{cosech}(\Theta)$$

Where the Θ term is a temperature, T , factor; the Φ term is a Debye-Waller factor and the \mathbf{I}_n are Bessel functions of the first kind.

1.2 Harmonic Systems

1.2.1 The Isotropic Harmonic Oscillator

In a chemical context vibrational spectroscopy covers the whole frequency range from a few wavenumbers upwards but is mostly concerned with the internal vibrations of the molecule. These have values, ca. 1000 cm^{-1} up to the highest stretching fundamental, the H-H stretch at 4400 cm^{-1} . These typical values can be compared with room temperature, $300\text{K} = 204 \text{ cm}^{-1}$. However the discrepancy is much more marked under real experimental conditions where the samples are cooled to 20K ($= 14 \text{ cm}^{-1}$). Such that

$$\Theta = \frac{\hbar\omega}{2k_B T} \approx \frac{1000}{14} \approx 70 \quad \therefore \text{coth}(\Theta) = 1.0 \quad \text{cosech}(\Theta) \ll 1.0$$

$$\Phi = \mathbf{Q}^2 \cdot \frac{\hbar}{2\mu\omega}$$

$$\Lambda \ll 1.0$$

Because the argument of the Bessel function is very small, it can be expanded

$$\mathbf{I}_n(\Lambda) = \frac{1}{n!} \left(\frac{\Lambda}{2} \right)^n$$

substituting into eq(1) yields the intensity expression for the isotropic harmonic oscillator.

$$S(\mathbf{Q}, n\omega) = \frac{(\mathbf{Q}^2 \cdot \mathbf{U}^2)^n}{n!} \cdot \exp(-\mathbf{Q}^2 \cdot \mathbf{U}^2)$$

This remarkably simple expression is a basis for understanding the INS intensities observed in scattering from molecules. Its simplicity does not derive from the application of any drastic approximations, indeed those used lead to errors which are much smaller than the presently attainable experimental errors.

Here, the conventional symbol for the Mean Square Displacement, U^2 , has been used.

$$U^2 = \frac{\hbar}{2m\omega} = \frac{16.759}{\mu \cdot \nu}$$

where U^2 is given in \AA^2 , the oscillator frequency, ν , is in cm^{-1} , and the mass, μ , in amu.

Remarks

The mass; in the case of a monatomic lattice the idea of mass can lead to no confusion. However in, even very simple, chemical systems there are many different atoms involved in the molecule's vibrations. In general all of the atoms in a molecule are involved in all of the vibrations except for special considerations of symmetry, of Group oscillations (eg -C=O), and of local oscillations (eg -CH overtones). Moreover, because of the predominant scattering cross-section of hydrogen it is the extent to which this atom is displaced during a vibration that is important. Almost certainly the mass, μ , will not be the atomic mass of hydrogen but somewhat more, dependent upon how many other heavier atoms are also involved in the motion. In the *ab-initio* programmes this is dealt with through the solution of the dynamical matrices, probably expressed in mass weighted coordinates [5].

The elastic line; occurs when no quanta of energy are exchanged between the neutron and the molecule, $n = 0$. (This corresponds to the Rayleigh line in Raman scattering.) The elastic line in INS is intense, decreases rapidly with momentum transfer and contains many complex contributions. It is very difficult to analyse this data and it is not directly observed in TOSCA spectra. It is given no further consideration here.

1.2.2 Fundamentals

Substituting for $n = 1$, in to the expression yields

$$S(\mathbf{Q}, \omega) = \mathbf{Q}^2 \cdot \mathbf{U}^2 \cdot \exp(-\mathbf{Q}^2 \cdot \mathbf{U}^2)$$

There are two idealised experiments; first, a constant Q^2 experiment, and; second, a constant ω experiment. In the first experiment the values of k_i and k_f are adjusted to maintain a constant Q^2 , two transitions are observed. The first is the elastic line and the second, at ω_0 , is the intensity associated with the excitation of the molecule into its first excited state, the fundamental. (For the advised reader it will be obvious that this Stokes transition is accompanied by an anti-Stokes transition, appearing at $-\omega_0$. However, because of the cryogenic experimental temperatures there are very few oscillators above the ground state, anti-Stokes bands are therefore very weak and are ignored.) In the second ideal experiment, at

the transition ω_0 , Q^2 is varied. Initially, at low values of Q^2 , the observed intensity increases and finally, at high values of Q^2 , the observed intensity falls away. This final fall is due to the Debye-Waller factor, $\exp(-2W) = \exp(-Q^2.U^2)$, whilst the original rise was given by the pre-exponential factor, $Q^2.U^2$. The position of intermediate maximum can be determined by differentiation,

$$S(Q, \omega) = S_{\max} \quad \text{at} \quad Q^2.U^2 = 1.$$

Spectrometers like TOSCA, with very small final energies, have $Q \sim ki$, therefore

$$Q^2.U^2 \approx k_i^2.U^2 = \frac{\nu}{2.0171(8.066)} \cdot \frac{16.759}{\mu.\nu} = 1. \quad \therefore \quad \mu = 1.$$

If the oscillator mass of the spectrum is unity then spectrometers like TOSCA are optimally designed to measure these spectra because, irrespective of the vibrational frequency, the maximum intensity is obtained.

1.2.3 Overtones

Overtones occur whenever the oscillator is excited from the ground state to levels above the first excited state. There is no unique route for the loss of two quanta by the neutron to a harmonic oscillator, the excitation of the sample by two single quanta ($2 \omega_0(0-1)$) is energetically equivalent to the excitation of the sample into its second excited state ($\omega_0(0-2)$). The strength of the overtone bands, S_n , can be obtained by substituting, $n > 1$. Fortunately, for spectrometers like TOSCA, the expressions simplify further for transitions above, say, 1000 cm^{-1} . [6]

$$S_n(Q, n\omega_0) \propto \frac{n^n}{n!} \left\{ \frac{1}{\mu} \cdot \exp\left(-\frac{1}{\mu}\right) \right\}^n$$

As can be seen the strength of the overtone sequence from heavier masses falls away dramatically as μ increases. Fortunately, the lower frequency fundamentals mostly involve heavier atoms and without this effect the low lying fundamentals would generate sequences that would completely overshadow higher fundamentals.

1.3 Anharmonicity

The vibrations of a molecule are ideally described as a system of independent oscillators. Breakdown of this approximation, involving the mixing of supposedly separate vibrational states, is one expression of anharmonicity. More commonly, even for systems that are well described as independent oscillators, the overtones do not fall at exact multiples of the fundamentals. Rather

$$\omega_0(0-n) = n.\omega_e.(1-(n+1)x)$$

In molecular systems this aspect of anharmonicity usually produces overtones at frequencies slightly lower than harmonic, ie the anharmonicity constant, x , is positive. The exchange of two individual quanta with a neutron is no longer equivalent to the exchange of a double quantum and structure will appear in the overtone band.

In this picture the internal vibrational spectra of molecules consists of a series of δ -functions representing the elastic line, $\delta(\omega)$, the n fundamentals, $\delta(\omega - \nu_n)$, and their overtones, eg $\delta(\omega - 3\nu_n)$,

$$S_{Int}(\mathbf{Q}, \omega) = \exp(-\mathbf{Q}^2 \cdot \mathbf{U}_{Int}^2) [\delta(\omega) + \delta(\omega - \nu_1) + \delta(\omega - \nu_2) + \dots \delta(\omega - \nu_n) \dots \delta(\omega - 2\nu_1) + \delta(\omega - 2\nu_2) + \dots \delta(\omega - 2\nu_n) \dots]$$

1.4 External Modes

So far only non-recoiling and isolated molecules have been considered. In the solid state molecules reside on their lattice sites and are prevented from recoiling, under the impact of the neutron, only by the forces which stabilise the crystal. These forces are responsible for the external modes of the molecule, ie modes that involve displacements of the undeformed molecule as a whole. The intermolecular forces are much weaker than the intramolecular forces the external, or lattice, vibrations have frequencies about 150 cm^{-1} . Similar to the internal vibrations the external vibrations, P_1 etc., can also be described by

$$S_{Ext}(\mathbf{Q}, \omega) = \exp(-\mathbf{Q}^2 \cdot \mathbf{U}_{Ext}^2) [\delta(\omega) + \delta(\omega - P_1) + \delta(\omega - P_2) + \dots \delta(\omega - P_n) \dots \delta(\omega - 2P_1) + \delta(\omega - 2P_2) + \dots \delta(\omega - 2P_n) \dots]$$

Combining these two expressions allows a description of the total scattering law

$$S_{Total} = S_{Trans} \otimes S_{Rot} \otimes S_{Vib} = S_{Ext} \otimes S_{Int}$$

$$S_{Total}(\mathbf{Q}, \omega) = \exp(-\mathbf{Q}^2 \cdot \mathbf{U}_{Int}^2) \cdot \exp(-\mathbf{Q}^2 \cdot \mathbf{U}_{Ext}^2) [\delta(\omega) [\delta(\omega) + \delta(\omega - P_1) + \dots \delta(\omega - nP_n) + \delta(\omega - \nu_1) [\delta(\omega) + \dots \delta(\omega - nP_n) \dots] + \delta(\omega - \nu_2) [\delta(\omega) + \dots \delta(\omega - nP_n) \dots] \dots]$$

Such that associated with each internal vibrational mode, ν_i , there is the full spectrum of external vibrations, the phonon-wings. (These will be familiar from UV spectroscopy where the internal vibrational spectrum appears as a wing on the allowed electronic transitions.) It should be noted that no change in the total INS intensity occurs but the vibrational transition no longer has a simple shape. Also [7]

$$S_{Total} = S_{Origin} + S_{Wing}$$

$$S_{Origin} = S_{Total} \cdot \exp(-\mathbf{Q}^2 \cdot \mathbf{U}_{Ext}^2)$$

Phonon wings have more or less complex shapes dependant upon how many orders have been excited. At the lowest values of Q only one phonon order has been excited; the band origin retains most of its intensity and the wing has a similar shape to the external mode spectrum. At higher Q values more phonon orders are excited producing complex wing shapes which are most often smooth and unfeatured but can be difficult to interpret. (The calculation of the vibrational intensities must be performed before the impact of phonon wings can be calculated. Therefore, we shall retain the convention of gas phase molecular spectroscopy and refer to all transitions as originating from internal modes, be they the one-quantum, fundamentals or more complex multi-quantum events.)

It is through the phonon-wings that neutron vibrational spectroscopy gives access to the internal and the external vibrational displacements, simultaneously and separately. [8]

$$U_{Total}^2 = U_{Ext}^2 + U_{Int}^2 = U_{Diffraction}^2 = B_{iso} / 8\pi^2$$

The intensity of the Bragg reflections observed in crystallographic determinations are governed by the same Debye-Waller factors introduced above. Such that a complete analysis of diffraction data will provide the same atomic MSD values, if measured at the same temperature. These are familiar as the anisotropic thermal ellipsoids commonly reported in contemporary crystallographic journals. Large external contributions to the total MSD suppress the experimental intensities in both diffraction and INS measurements and the best work is always conducted at cryogenic temperatures.

The total MSD's obtained by diffraction and INS do not always agree and, usually, the diffraction value is the larger. This discrepancy is generally caused by the static-disorder of molecules occupying several alternative positions of about equal thermodynamic stability. The atomic positions are dispersed in real space and the scattering factors are no longer in phase. This has the same effect as changing the atomic positions dynamically. There is a loss of Bragg intensity, which is easily mistaken for a large MSD value. In very favourable cases this disorder can be detected and incorporated into the final structural model. In less favourable cases a severely anisotropic shape or the large size of the thermal ellipsoid will strongly suggest the presence of an unresolved disorder. In unfavourable cases it passes undetected. The result of structural disorder is always to exaggerate the value of the MSD's as obtained from diffraction experiments.

1.5 Real Systems

1.5.1 Anisotropy

Isotropic harmonic oscillators are chemically rare, most systems involve significant anisotropy's resulting from the presence of stretching, eg -CH 3000 cm⁻¹, bending, eg -CH₂ 1400 cm⁻¹, and deformation modes, eg C-C-C 800 cm⁻¹, in the same molecule.

1.5.2 Aligned Oscillators

After isotropy, the next simplest case has all the oscillators vibrating in the same direction. This implies that there is only one type of lattice site for the molecule and all the molecules are parallel. Restating the scattering law for a vibrational displacement U , exclusively in the direction x , occurring at the associated frequency ν_i .

$$S(\mathbf{Q}, \nu_i) = (\mathbf{Q} \cdot \mathbf{U}_i)^2 \cdot \exp(-(\mathbf{Q} \cdot \mathbf{U}_i)^2)$$

$$(\mathbf{Q} \cdot \mathbf{U}_i)^2 = (Q U_i \cdot \cos(\varphi))^2 = (\mathbf{Q} \mathbf{Q} : \mathbf{U}_i \mathbf{U}_i)$$

$$\mathbf{U}_i \mathbf{U}_i^T = \begin{bmatrix} U_i \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} U_i & 0 & 0 \end{bmatrix} = {}_j \mathbf{B}_{\nu_i} \quad ; \quad \mathbf{Q} \mathbf{Q}^T = Q^2 \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} x & y & z \end{bmatrix}$$

Here our nomenclature is modified to cover the presence of more than one vibrational mode of more than a single scattering atom and to agree with present literature practice. The MSD tensor of the scattering atom, j , in the vibrational mode, i , at frequency, ν_i , is ${}_j \mathbf{B}_{\nu_i}$. Only the component of \mathbf{Q} along \mathbf{U} is effective and the *dot* product of the vectors \mathbf{Q} and \mathbf{U} is required. (This equation also defines the vector transpose operation, ^T.) If the \mathbf{Q} is entirely parallel to \mathbf{U} (ie $\varphi = 0$), S is maximised. If there is no component of \mathbf{Q} parallel to \mathbf{U} (ie $\varphi = 90$), S is zero. In this respect the selection rules of neutron scattering are similar to the electric vector selection rules of ir spectroscopy. Samples of aligned oscillators in single crystals large enough for neutron beams are rare and more typically only powders are available. In experiments on powders the relative directions of the vibrational displacements and the momentum transfer vector are not fixed but lie at random. The scattering law must be averaged for all directions in space. The total internal MSD tensor of the atom is ${}_j \mathbf{A}_{internal}$ and the powder averaged result is given by [9];

$${}_j S(\mathbf{Q}, \nu_i) = \langle \mathbf{Q} \mathbf{Q} : {}_j \mathbf{B}_{\nu_i} \cdot \exp(-\mathbf{Q} \mathbf{Q} : {}_j \mathbf{A}) \rangle_{\text{Powder}}$$

Where,

$${}_j \mathbf{B}_{\nu_i} = {}_j \mathbf{U}_{\nu_i} \cdot {}_j \mathbf{U}_{\nu_i}^T$$

$${}_j \mathbf{A}_{internal} = \sum_i {}_j \mathbf{B}_{\nu_i}$$

Powder averages can be calculated in several ways;

1. in the cases of strictly oblate or prolate MSD's, precise analytical expressions exist [10] but lack generality;
2. numerical averaging techniques are very general [11] but tend to be slow if precision is required;
3. approximate methods are general, rapid and reasonably accurate [9].

The aCLIMAX program uses the 'almost-isotropic approximation' [9] it provides accurate averages when applied to MSD's that are not too anisotropic. (The errors are ca. 5% if the ratio of the minor to major axes of the thermal ellipsoid is three or less but may approach 20% if, exceptionally, the ratio exceeds five).

Three important consequences follow from powder averaging; first, all vibrations have some component parallel to \mathbf{Q} and are therefore observable; second, the intensity of each fundamental is weakened by a factor three; third, combination bands are observable. Combination bands occur when \mathbf{Q} has components along more than one vibrational direction.

1.6 Working equations

Here we present the equations used in aCLIMAX to calculate the INS spectrum from Gaussian output for fundamentals and overtones, or combinations, to the fourth order.

Appropriate Spectrometers

The aCLIMAX program is specifically written to analyse data obtained on the TOSCA spectrometer at the ISIS facility, The Rutherford Appleton Laboratory, UK. However, TOSCA is very similar in its operational characteristics to several other spectrometers (see section 1.2.2 and links through [1]) and, within this limitation, the calculated results should be generally applicable.

The values of momentum transfer, Q , are calculated according to

$$Q^2 = k_i^2 + k_f^2 - 2.k_i.k_f.Cos(\theta); \quad k_i^2 = \frac{\nu + \omega}{2.0717(8.066)}; \quad k_f^2 = \frac{\omega}{2.0717(8.066)}$$

Where, on TOSCA, the scattering angle is (either 45°, or) 135° and the final neutron energy, ω , is 32 cm⁻¹.

Gaussian output

The MSD calculated in Gaussian '98, and incidentally most other normal coordinate programs, are given in the mass-weighted coordinate system and the sum of all atomic displacements in any normal mode is normalised.

$$U_{vi}^2 = \sum_j^{Tr} C_{vi} = 1$$

$${}_j C_{vi} = {}_j B_{vi \cdot j} M^{-1}$$

To recover the atomic displacements in conventional units, Å, from the normalised displacement vectors, ${}_j c$, given by Gaussian, where ${}_j M$ is the mass of the j^{th} atom in amu;

$${}_j c_{vi \cdot j} c_{vi}^T = {}_j C_{vi}$$

$${}_j B_{vi} = {}_j C_{vi \cdot j} M \cdot \frac{16.759}{\nu_i}$$

The principal working equation in aCLIMAX is based on the need to treat data taken from powders and it cannot treat experimental results from single crystals. (Where Tr implies that the trace of the matrix representation of the tensor has been taken, this operation yields the scalar magnitude of the tensor. The \cdot symbol implies contraction of the two tensors, in matrix representation this is achieved by performing the trace operation on the product of the two matrices.) Here we also introduce the weightings associated with the scattering crosssections of the different atoms, ${}_j \sigma$.

1.6.1 One-quantum events

$${}_j S(Q, \nu_i) = \frac{Q^2 \cdot \text{Tr} \mathbf{B}_{\nu_i}}{3} \cdot \exp(-Q^2 \cdot {}_j \alpha_{\nu_i}) \cdot {}_j \sigma$$

$${}_j \alpha_{\nu_i} = \frac{1}{5} \left\{ \text{Tr} {}_j \mathbf{A} + \frac{2({}_j \mathbf{B}_{\nu_i} : {}_j \mathbf{A})}{\text{Tr} \mathbf{B}_{\nu_i}} \right\}$$

$$S(\nu_i)_{Total} = \sum_j {}_j S(Q, \nu_i)$$

1.6.2 Two-quantum events

$${}_j S(Q, \nu_{i,k}) = {}_j S(Q, \nu(0-2)) \quad ; i = k$$

$$= \frac{Q^4}{30} \cdot \left\{ \text{Tr} \mathbf{B}_{\nu_i} \cdot \text{Tr} \mathbf{B}_{\nu_i} + 2 \cdot ({}_j \mathbf{B}_{\nu_i} : {}_j \mathbf{B}_{\nu_i}) \right\} \exp(-Q^2 \cdot {}_j \beta) \cdot {}_j \sigma$$

$${}_j S(Q, \nu_{i,k}) = {}_j S(Q, \nu(0-1,0-1)) \quad ; i \neq k$$

$$\frac{Q^4}{15} \cdot \left\{ \text{Tr} \mathbf{B}_{\nu_i} \cdot \text{Tr} \mathbf{B}_{\nu_k} + {}_j \mathbf{B}_{\nu_k} : {}_j \mathbf{B}_{\nu_i} + {}_j \mathbf{B}_{\nu_i} : {}_j \mathbf{B}_{\nu_k} \right\} \exp(-Q^2 \cdot {}_j \beta) \cdot {}_j \sigma$$

$${}_j \beta \approx \frac{\text{Tr} \mathbf{A}_{Ext}}{3}$$

$$S(\nu_{i,k})_{Total} = \sum_j {}_j S(Q, \nu_{i,k})$$

The first-overtones (0-2) and combinations (0-1, 0-1') and (0-1', 0-1) are enumerated separately. Here we adopt the isotropic approximation for the Debye-Waller factor, an 'almost-isotropic' approximation for β exists [9] but it is unnecessarily cumbersome.

1.6.3 Three-quantum events

$${}_j S(Q, \nu_{i,k,l}) =$$

$$\frac{9 \cdot Q^6}{543} \cdot \left\{ \text{Tr} \mathbf{B}_{\nu_i} \cdot \text{Tr} \mathbf{B}_{\nu_k} \cdot \text{Tr} \mathbf{B}_{\nu_l} \right\} \exp(-Q^2 \cdot {}_j \beta) \cdot {}_j \sigma$$

$${}_j \beta \approx \frac{\text{Tr} \mathbf{A}_{Ext}}{3}$$

$$S(\nu_{i,k,l})_{Total} = \sum_j {}_j S(Q, \nu_{i,k,l})$$

1.6.4 Four-quantum events

$${}_j S(Q, \nu_{i,k,l,m}) = \frac{27 \cdot Q^8}{9850} \left\{ \text{Tr} \mathbf{B}_{\nu_i} \cdot \text{Tr} \mathbf{B}_{\nu_k} \cdot \text{Tr} \mathbf{B}_{\nu_l} \cdot \text{Tr} \mathbf{B}_{\nu_m} \right\} \exp(-Q^2 \cdot {}_j \beta) \cdot {}_j \sigma$$

$${}_j \beta \approx \frac{\text{Tr} \mathbf{A}_{Ext}}{3}$$

$$S(\nu_{i,k,l,m})_{Total} = \sum_j {}_j S(Q, \nu_{i,k,l,m})$$

1.6.5 Phonon Wings

In the same way that the total displacements of an atom due to internal modes can be written in tensor form, ${}_j \mathbf{A}_{internal}$, so too can the external contributions, ${}_j \mathbf{A}_{External}$. The various methods of obtaining the individual matrix elements are described below, see section 1.7. Further, the almost-isotropic approximation can be applied to the calculation of the phonon wing intensity. Notice that the individual contribution of each atom is treated independently since each atom moves, for any given internal vibration, in a specific direction with respect to its external tensor. Moreover the external tensor of one particular atom will only equal that of another atom if they are related through the crystalline symmetry.

$${}_j S(\nu_i)_o = {}_j S(\nu_i) \cdot \exp(-Q^2 \cdot {}_j \alpha_{Ext})$$

$${}_j \alpha_{Ext} = \frac{1}{5} \left\{ \text{Tr} \mathbf{A}_{Ext} + 2 \cdot \left(\frac{{}_j \mathbf{B}_{\nu_i} \cdot {}_j \mathbf{A}_{Ext}}{\text{Tr} \mathbf{B}_{\nu_i}} \right) \right\}$$

$${}_j S(\nu_i)_{Wing} = {}_j S(\nu_i) - {}_j S(\nu_i)_o$$

$$S(\nu_i)_o = \sum_j {}_j S(\nu_i)_o ; \quad S(\nu_i)_{Wing} = \sum_j {}_j S(\nu_i)_{Wing}$$

These expressions are strictly valid only for spectrometers working at constant-Q, which is obviously not the case for TOSCA. The intensity of the band origin, S_o , should, however, be reasonably well approximated since these are relatively sharp in frequency and hence in Q. The intensity of the wing, S_w , is underestimated since, as the wing develops, it reflects the strength of a band origin measured at slightly greater Q. This is mitigated somewhat by the method of calculating the distribution of the wing intensity among the several phonon orders. Ten orders of phonon expansion are used in a-CLIMAX and the strength of the p^{th} order is [12]

$$I_p = \frac{(Q_{p \cdot j}^2 \alpha_{Ext})^p}{p!} \cdot \exp(-Q_{p \cdot j}^2 \alpha_{Ext})$$

$$\sum_1^{10} I_p = S(v_i)_{Wing}$$

The value of Q_p is determined from sum of the transition frequency of the parent internal mode and the weighted mean frequency of the p^{th} phonon wing. This ensures that the intensity distribution in wings is weighted towards the higher phonon orders.

1.6.5.1 Construction of the Phonon Wing Shape

Only one wing shape is available in aCLIMAX for all atoms and this may not be appropriate for complex systems. Nonetheless any deviations are unlikely to be severe since the shape of the one-phonon wing is generally found to be unimportant. However, it should be born in mind as a possible explanation for complex spectral features. Any wing shape that can be constructed is acceptable but surprisingly good results are obtained from even the simplest shapes. The shape of the one-phonon spectrum is convoluted with itself to form the shape of the second, this is convoluted with the one-phonon to give the third, etc. to the tenth order. Irrespective of the shape of the one-phonon wing the higher orders rapidly revert to gaussian forms. The area of each of the phonon orders is initially normalised to unity. Their final individual weights are dependent on the position of the parent band origin and were discussed above.

1.7 Standard Approaches to the estimation of External Atomic Displacements.

1.7.1 Analysis of Crystallographic data.

Modern crystallography is often performed at low temperatures to reduce the impact of the Debye-Waller factor on the observed intensities and the resulting crystallographic data is analysed to yield the total atomic displacements (or thermal parameters, or anisotropic displacement parameters). If the published ellipsoids are given in conventional units ($\text{\AA}^2 \times 10^4$) and referred to the molecular geometry they can be readily exploited. Unfortunately, although the units are conventional the ellipsoids are almost always given in respect of the reciprocal lattice and as such cannot be easily exploited. The reported data must be transformed onto the molecular frame.

Occasionally crystallographic data are treated to a rigid body analysis. In this procedure, after making some allowance for the internal displacements of the atoms, the external displacements have been analysed in terms of torsions about the principal axes of inertia and vibrations along these axes. These are conventionally given as the **L**, **T** and **S** tensors [8], and can be used to provide the ${}_j\mathbf{A}_{External}$ tensors.

1.7.2 Sachs-Teller mass tensor

In most molecules hydrogen atoms of chemical compounds, generally, lie away from the centre of mass and have significant radii of gyration, R_g . Since neutrons interact with these hydrogen atoms the neutron experiences the full rotational inertia, I , of the molecule. Naturally the neutron also experiences the linear inertia (or mass) of the whole molecule, M_{Mol} . The effective mass, therefore, changes as the neutron's impact angle at the target atom,

i , changes. Its average value can be expressed as a tensor, the Sachs-Teller mass tensor. Where the atomic masses are given in amu and distances in Å.

$${}_j\mathbf{M}_{ST}^{-1} = \frac{1}{{}_jM_{ST}} = \left\{ \frac{{}_jR_g^2}{I} \right\} + \left\{ \frac{1}{M_{Mol}} \right\}$$

$${}_j\mathbf{M}_{ST}^{-1} = \left[\begin{array}{ccc} \left(\frac{y_j^2}{I_z} + \frac{z_j^2}{I_y} \right) & \frac{-y_jx_j}{I_z} & \frac{-z_jy_j}{I_x} \\ \frac{-x_jy_j}{I_z} & \left(\frac{x_j^2}{I_z} + \frac{z_j^2}{I_x} \right) & \frac{-z_jx_j}{I_y} \\ \frac{-x_jz_j}{I_y} & \frac{-y_jz_j}{I_x} & \left(\frac{y_j^2}{I_x} + \frac{x_j^2}{I_y} \right) \end{array} \right] + \left[\begin{array}{ccc} \frac{1}{M_{Mol}} & 0 & 0 \\ 0 & \frac{1}{M_{Mol}} & 0 \\ 0 & 0 & \frac{1}{M_{Mol}} \end{array} \right]$$

$${}_i\mathbf{M}_{ST}^{-1} = \left\{ \frac{1}{M_I} \right\} + \left\{ \frac{1}{M_{Mol}} \right\} = {}_i\mathbf{M}_I^{-1} + {}_i\mathbf{M}_T^{-1}$$

We also define the reciprocal lattice-frequency tensors, for librational frequencies of the molecule about its principal axes, ν_I^{-1} , or along its axes, ν_T^{-1} .

$$\nu_I^{-1} = \left[\begin{array}{cc} \frac{1}{\nu_x} & 0 \\ & \frac{1}{\nu_y} \\ 0 & & \frac{1}{\nu_z} \end{array} \right]_I ; \quad \nu_T^{-1} = \left[\begin{array}{cc} \frac{1}{\nu_x} & 0 \\ & \frac{1}{\nu_y} \\ 0 & & \frac{1}{\nu_z} \end{array} \right]_T$$

The individual frequencies should be related to spectral features observed in the external mode spectrum of the sample, or might be regarded as simply fitting parameters. This approach is a naïve expansion of the Einstein Oscillator approximation to the dynamics of monatomic lattices, here 6 frequencies are allowed.

Then

$${}_j\mathbf{U}_I^2 = (16.759) \cdot {}_j\mathbf{M}_I^{-1} \cdot \nu_I^{-1} ; \quad {}_j\mathbf{U}_T^2 = (16.759) \cdot {}_j\mathbf{M}_T^{-1} \cdot \nu_T^{-1}$$

$${}_j\mathbf{U}_{ST}^2 = {}_j\mathbf{U}_I^2 + {}_j\mathbf{U}_T^2 = {}_j\mathbf{A}_{External}$$

1.7.2.1 The isotropic field approximation

The full use of the Sachs-Teller approach allows a more realistic modelling of the crystalline environment but if it were truly needful a full molecule in lattice calculation is better. A more useful approximation is often to ignore the complications of a full S-T treatment and set all the external forces to be equal [15]. Under this regime the response of the molecule to scattering is to be displaced about its principal axes of inertia in inverse proportion to the moments of inertia and along the axes inversely in respect of its molecular mass. Thus

$${}_j \mathbf{A}_{external} \propto \begin{bmatrix} \frac{1}{I_a} & & 0 \\ & \frac{1}{I_b} & \\ 0 & & \frac{1}{I_c} \end{bmatrix} + \begin{bmatrix} \frac{1}{M} & & 0 \\ & \frac{1}{M} & \\ 0 & & \frac{1}{M} \end{bmatrix}; \quad {}_j \mathbf{A}_{external} \propto I^{-1}$$

Non-spherical, or anisotropic, components appear only if $I_a \neq I_b \neq I_c$, and the translational, $1/M$, contribution is strictly isotropic. Moreover, translational modes appear at the lowest frequencies and their contributions are small. In this approximation these small, isotropic, translational components are subsumed within the librational effects. This gives the ratios of the leading terms in the external tensor but it remains to know their sum.

Application of the isotropic approximation to the experimental observations can provide an estimate of ${}_j \mathbf{A}_{External}$. Choosing a suitable vibrational transition, in an uncongested region around 500 - 600 cm^{-1} , measure the band origin intensity, S_O , and that of its wing, S_W , the magnitude of ${}_i \mathbf{A}_{External}$ is;

$$\text{Tr} {}_j \mathbf{A}_{External} \approx \frac{-3}{Q^2} \cdot \ln \left(\frac{S_{Origin}}{S_{Total}} \right)$$

(Here the working equation of section 1.6.5 has been rearranged.) Knowing the magnitude of the tensor and the ratios of the individual components on the diagonal allows a first approximation to the tensor to be constructed. In practice, when using aCLIMAX, the initial value of $\text{Tr} {}_i \mathbf{A}_{External}$ is often estimated by inspection, varying the value used in the calculation until the calculated spectrum becomes an acceptable representation of the observed spectrum.

1.7.3 Recoil

In soft solids at low temperatures, and all systems at high enough temperatures, molecules may experience little hindrance to local diffusion. The transfer of even modest momentum will result in the excitation of all phonon orders. The peak of the elastic line intensity moves to higher energies as the momentum transferred increases. In the vibrational region the wing component of the vibrational transition now contains all of the observed intensity and the intensity remaining at the origin has completely disappeared. Fortunately the band shape simplifies to become a broad gaussian but it peaks at energies considerably above the band origin. The final state of the molecule is above the potential restoring its equilibrium position, ie it has been excited into the continuum of external modes. This final state is similar to that of molecules in the gas and the molecule is said to have recoiled [16]. The separation between the recoil band and origin is determined by the effective mass and the momentum transferred.

In the case of monatomic systems (or for energy transfers in excess of several eV) the effective mass is the atomic mass. However, for atoms in molecules (excited to typical thermal energies) the atomic mass is irrelevant, since the molecule responds as an undeforming body.

Therefore, for convenience, we define an average Sachs-Teller Mass to be applied to all spectral features irrespective of which of the n atoms scattered the neutron. On spectrometers like TOSCA, this mass controls the final position, ν_R , of the recoiled band in respect of the band origin, ν_0 .

$$\bar{M}_{ST}^{-1} = \frac{1}{3n} \cdot \sum_j^T [{}_j \mathbf{M}_{ST}^{-1}]$$

$$\nu_R = \nu_0 \cdot \bar{M}_{ST}^{-1}$$

The width of the gaussian shaped recoil-band is determined by the lattice frequencies and is usually treated as a fitting parameter.

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