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## TRANSFORM RELATIONSHIP BETWEEN ABSORPTION AND RESONANCE RAMAN SCATTERING IN INHOMOGENEOUS MEDIA

(Presented by Ch. Lushchik)

**Abstract.** A relationship between the absorption spectrum and the corresponding Raman excitation spectrum of molecules/impurity centers in inhomogeneous media has been derived for the case when the inhomogeneous broadening is smaller than the homogeneous one. This is a generalization of the basic transform relationship found earlier for an ensemble of identical molecules.

### 1. Introduction

Resonance Raman scattering (RRS) offers a sensitive method for studying the coupling between electronic and vibrational states in molecules and impurity centres in crystals. In traditional interpretation of the Raman process, the system absorbs the incident photon by a transition to the "virtual" state and then emits the scattered photon on transition to a final state, which differs in vibrational excitation from the initial state. The development of the molecular Raman scattering theory started already in 1925 with the dispersion relationships found by Kramers and Heisenberg [1]. Despite the long history, there are numerical and conceptual problems with the Kramers-Heisenberg theory. It is a sum-over-states treatment, involving a direct numerical summation over the explicit intermediate ("virtual") vibronic states, which becomes rapidly intractable as the number of modes increases. Besides, the processes of photon absorption and reemission as distinct events on the time scale have no reflection in this frequency-domain formulation. Because of that, a time-dependent representation of the Heisenberg-Kramers formula (as a triple integral in the time domain) was proposed [2,3], analogous to Lax's formulation of the absorption theory [4]. This idea was developed into the time correlation theory of resonance secondary emission, a unified theory of scattering and luminescence, including the Rayleigh and the Raman scattering, ordinary and hot luminescence. The Raman scattering is the part of the whole secondary radiation emitted at the beginning of the vibrational relaxation process in the excited electronic state. The spectrum of RRS can be represented via an expansion of photon correlation functions which determine the Fourier transform of optical absorption. So it appears that these two different (from a viewpoint of experiment) phenomena — absorption and RRS — can be not only described by a common theory but are also related via transform relationships.

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This was also a solution of the multimode problem in the RRS theory. The problem is: though in the scattering process only one mode is finally excited (speaking about the first order RRS), all the other Franck-Condon active modes take part in this process, i. e. all the transitions of absorption are also included in RRS. Therefore, the characteristics of RRS on every Raman-active mode depend, in principle, on all the parameters of vibronic coupling. In a multimode case, as e. g. large organic molecules or impurity centers in crystals, one should take into account a large number of parameters to get information about the coupling with the Raman-active mode. Because of that for multimode system detailed models are used which take into account all the data got by different methods. Because of a large number of parameters the results obtained by different groups do not coincide. In particular, the traditional approach fails in the case of systems with quasicontinuous electronic-vibrational spectra.

To overcome these problems a transform method was proposed which relates the Raman excitation profiles (REPs), i. e. the variation of a mode's Raman scattering intensity as the excitation is tuned through the optical absorption, to the experimentally recorded absorption spectrum [2,5]. So, all the Franck-Condon active modes which are not Raman-active but give contribution to REP, are taken into account via absorption. The concrete form of the relationship depends on the model of the vibronic coupling.

In the case of the basic model, when there is a single vibronic effect on the electronic transition — the displacement of equilibrium positions of vibrating nuclei, the transform relationship was derived already in 1967 [2]. According to this formula the shape of REP is determined by subtraction of the transformed absorption spectra, i. e. by the interference of functions of complex susceptibility (refractive index) in frequencies of excitation and scattering. In this model, the frequency dependence of REP is obtained without any parameter. The single parameter of Stokes losses on the Raman-active mode determines the absolute value of the intensity of the Raman line. All the other vibronic effects are taken into account via the experimental absorption spectrum.

Further the transform method was elaborated for the consideration of additional vibronic effects such as the Herzberg-Teller interaction [6,7] (the violation of the Condon approximation), the quadratic Franck-Condon interaction [8-10] (the change of vibrational frequencies and the mixing of normal coordinates on the electronic transition), the Jahn-Teller effect [11,12] (the degeneracy of electronic states). Here we take into account the inhomogeneity of the medium when the absorption and the emission spectra exhibit inhomogeneous broadening.

## 2. The transform relationship for the basic model

Before deriving the transform relationship for molecules in inhomogeneous media, let us start with the simplest model and demonstrate first a trivial way of deriving the transform relationship for the case of identical molecules\*\*. In this model the following standard assumptions are made: 1) a single excited electronic state, 2) the adiabatic and the Condon approximation, 3) harmonic vibrations and 4) linear electron-vibrational coupling (the only vibronic effect is the displacement of the equilibrium positions of nuclei). Then the absorption spectrum at  $T=0$  is defined as

\*\* The derivation of the basic transform relationship given below is really oversimplified, as it ignores the temperature and polarization effects. One can find the derivation of the transform relationship with the consideration of these effects, e. g. in [2, 9, 11] where the Fourier transform technique is used.

$$I_{\text{abs}}(\omega_0) = \text{const } \omega_0 \text{Im} \sum_{m=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 0 \rangle}{\omega_0 - \Omega_{21} - \omega m - i\Gamma_m}, \quad (1)$$

where  $\omega_0$  denotes the frequency of excitation;  $\Omega_{21}$ , the frequency of the pure-electronic (zero-phonon) transition; 0 and  $m$  stand for initial and intermediate vibrational states;  $\omega$  is the vibrational frequency;  $\Gamma_m$ , the total (homogeneous) damping constant of the state  $m$ . The Raman amplitude of the first order scattering process can be written as

$$\alpha_{0 \rightarrow 1}(\omega_0) = \sum_{m=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 1 \rangle}{\omega_0 - \Omega_{21} - \omega m - i\Gamma_m}. \quad (2)$$

(Below an additional assumption  $\Gamma_m = \Gamma = \text{const}$  is made.) Using the properties of a harmonic oscillator, we obtain for the Franck-Condon factors

$$\langle 0 | m \rangle = e^{-\xi^2/2} \xi^m / \sqrt{m!}, \quad (3a)$$

$$\langle m | 1 \rangle = e^{-\xi^2/2} \xi^{m+1} \sqrt{m!} \left\{ \frac{1}{m!} - \frac{\xi^{-2}}{(m-1)!} \right\}, \quad (3b)$$

where  $\xi$  is a dimensionless displacement parameter for the Raman-active mode and it is related to the displacement expressed in massweighted coordinates through  $\Delta Q = (2\hbar/\omega)^{1/2} \xi$ . Substituting Eqs. (3) into Eq. (2), the imaginary part of the Raman amplitude is defined as

$$\text{Im } \alpha_{0 \rightarrow 1} = e^{-\xi^2} \Gamma \sum_{m=0}^{\infty} \frac{\xi^{2m+1}/m! - \xi^{2m-1}/(m-1)!}{(\Omega_{21} + \omega m - \omega_0)^2 + \Gamma^2}.$$

The first term in the nominator is proportional to the absorption spectrum

$$e^{-\xi^2} \Gamma \sum_{m=0}^{\infty} \frac{\xi^{2m+1}/m!}{(\Omega_{21} + \omega m - \omega_0)^2 + \Gamma^2} \sim \xi I_{\text{abs}}(\omega_0)/\omega_0$$

multiplied by the parameter of shift  $\xi$ . The second term

$$\begin{aligned} & e^{-\xi^2} \Gamma \sum_{m=1}^{\infty} \frac{\xi^{2m-1}/(m-1)!}{(\Omega_{21} + \omega m - \omega_0)^2 + \Gamma^2} = \\ & = e^{-\xi^2} \Gamma \xi \sum_{n=0}^{\infty} \frac{\xi^{2n}/n!}{(\Omega_{21} + \omega n + \omega - \omega_0)^2 + \Gamma^2} \sim \xi I_{\text{abs}}(\omega_0 - \omega)/\omega_0 \end{aligned}$$

is proportional to the absorption spectrum shifted to the frequency of the Raman-active mode  $\omega$ ;  $\omega_0 - \omega = \Omega$ , the scattering frequency. So, we have found that the imaginary part of the Raman amplitude is determined by the interference of the absorption spectrum in the excitation and the scattering frequency:

$$\text{Im } \alpha(\omega_0) = \xi (I_{\text{abs}}(\omega_0) - I_{\text{abs}}(\Omega))/\omega_0.$$

The real part can be calculated by using the Kramers-Kronig transform relationship which relates the real part of the complex refractive index  $\text{Re } \Phi(\omega_0)$  to the imaginary part of it,  $\text{Im } \Phi(\omega_0) = I_{\text{abs}}(\omega_0)/\omega_0$ ,

$$\text{Re } \Phi(\omega_0) = (i/\pi) P \int_{-\infty}^{\infty} dx \frac{\text{Im } \Phi(x)}{x - \omega_0}. \quad (4)$$

As a result we obtain for the Raman amplitude

$$\alpha_{0 \rightarrow 1} \sim \xi [\Phi(\omega_0) - \Phi(\omega_0 - \omega)], \quad (5)$$

where

$$\Phi(\omega) = i\pi I_{\text{abs}}(\omega) / \omega + P \int_{-\infty}^{\infty} dx \frac{I_{\text{abs}}(x) / x}{x - \omega} \quad (6)$$

is the function of complex susceptibility (refractive index). Eq. (5) gives for the Raman excitation spectrum

$$I(\omega_0) \sim \xi^2 |\Phi(\omega_0) - \Phi(\Omega)|^2. \quad (7)$$

We can see that in this model the frequency dependence of scattering is determined solely by the spectral form of the absorption spectrum. The displacement of the Raman-active mode enters only as a simple scaling factor of the cross section.

So, having the experimentally recorded absorption spectrum  $I_{\text{abs}}(\omega_0)$ , the function  $\Phi(\omega)$  can be calculated according to Eq. (6). Then the REPs of Raman-active modes can be found by using Eq. (7) and compared with the experimental ones. The transform relationship can be used for determination of the vibronic parameters of Raman-active modes as well as a criterion of the model chosen for a given molecule.

### 3. The transform relationship for inhomogeneous media

The transform relationship given above works only in case of the ensemble of identical molecules. Molecules in solutions and inhomogeneous matrices are affected by inhomogeneously distributed perturbations, which can be taken into account via averaging over the spectra. Below the following approximations are made when examining the effect of the inhomogeneous broadening.

1) It is assumed that the inhomogeneities of the host matrix are static, i.e. they do not depend on time. Such an assumption can be used when the frequency of the perturbation change is smaller than width of the lines in the spectrum under selective excitation.

2) The inhomogeneities affect the energy of the electronic transition in the molecule but do not change its local dynamics. The fluctuations of the electronic energy usually exceed those of the vibrational frequencies.

In these approximations the spectrum with inhomogeneous broadening is determined by the integral

$$I(\omega_0) = \int_{-\infty}^{\infty} d\Omega_{21} \varrho(\Omega_{21}) I(\omega_0, \Omega_{21}), \quad (8)$$

where  $\varrho(\Omega_{21})$  is the distribution of molecules/luminescence centers as a function of the electronic transition energy  $\Omega_{21}$ .  $I(\omega_0)$  depends on the shape of the homogeneous spectrum  $I(\omega_0, \Omega_{21})$  as well as on the distribution function  $\varrho(\Omega_{21})$ . Below the latter is chosen in the Gaussian approximation

$$\varrho(\Omega_{21}) = \frac{1}{\sqrt{2\pi} \Delta} \exp \left\{ -\frac{(\Omega_{21} - \bar{\Omega}_{21})^2}{2\Delta^2} \right\}. \quad (9)$$

( $\bar{\Omega}_{21}$  is the average frequency of the pure-electronic transition,  $\Delta$  is the inhomogeneous width). As shown in [13], the Gaussian distribution works well in case of molecules in solutions.

Let us use for homogeneous spectra the basic model, i.e. the absorption is defined by Eq. (1) and the RRS intensity, by the squared amplitude (2),

$$I(\omega_0) = \sum_{m,m'=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 1 \rangle}{\omega_0 - \Omega_{21} - \omega_m + i\Gamma_m} \frac{\langle 1 | m' \rangle \langle m' | 0 \rangle}{\omega_0 - \Omega_{21} - \omega_{m'} - i\Gamma_{m'}} =$$

$$= \sum_{m,m'=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 1 \rangle \langle 1 | m' \rangle \langle m' | 0 \rangle}{\omega_{m'} - \omega_m - i(\Gamma_m + \Gamma_{m'})} \left[ \frac{1}{\omega_0 - \Omega_{21} - \omega_m + i\Gamma_m} - \frac{1}{\omega_0 - \Omega_{21} - \omega_{m'} + i\Gamma_{m'}} \right]. \quad (10)$$

In the case of Gaussian inhomogeneous distribution (9) the following integral should be calculated

$$\int_{-\infty}^{\infty} d\Omega_{21} e^{-\Omega_{21}^2/2\Delta^2} \frac{1}{\omega_0 - (\Omega_{21} + \bar{\Omega}_{21}) - \omega_m \mp i\Gamma_m} =$$

$$= \mp i\pi \exp [(\Gamma_m \mp ix_m)^2/2\Delta^2] \left[ 1 - \operatorname{erf} \left( \frac{\Gamma_m \mp ix_m}{\Delta\sqrt{2}} \right) \right]$$

where  $x_m = \omega_0 - \bar{\Omega}_{21} - \omega_m$ , a  $\operatorname{erf}(z) = (2/\sqrt{\pi}) \int_0^z dx e^{-x^2}$ . Further we use

the dimensionless value  $z_m = (\Gamma_m \mp ix_m)/\Delta\sqrt{2}$ . We obtain for the inhomogeneous absorption spectrum

$$I_{\text{abs}}(\omega_0) \sim \frac{\sqrt{\pi}}{\Delta\sqrt{2}} \sum_{m=0}^{\infty} |\langle 0 | m \rangle|^2 \operatorname{Re} \left\{ \exp(z_m^2) [1 - \operatorname{erf}(z_m)] \right\} \quad (11)$$

and for the inhomogeneous REP

$$I(\omega_0) = i \frac{\sqrt{\pi}}{\Delta\sqrt{2}} \sum_{m,m'=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 1 \rangle \langle 1 | m' \rangle \langle m' | 0 \rangle}{z_m + z_{m'}^*} \times$$

$$\times \left\{ \exp(z_m^2) [1 - \operatorname{erf}(z_m)] + \exp(z_{m'}^{*2}) [1 - \operatorname{erf}(z_{m'}^*)] \right\}. \quad (12)$$

One can see that inhomogeneity exhibits itself in different ways in the absorption and REP. The intensity distribution in the absorption spectrum is determined by the Franck-Condon factors, the inhomogeneous broadening only changes the band shape (cf. (1) and (11)). In a general case REP cannot be related to the absorption by a simple transformation relationship because of the denominator in Eq. (12). However, if the inhomogeneous broadening is smaller than the homogeneous one ( $\Delta \ll \Gamma_m \Rightarrow z_m$  is large), i.e. the vibrational relaxation processes dominate over the inhomogeneous broadening, the asymptotic expansion of  $\operatorname{erf}(z)$  can be used:

$$\operatorname{erf}(z) = 1 - \frac{1}{\pi} e^{-z^2} \sum_{k=0}^{\infty} (-1)^k \frac{\Gamma(m+1/2)}{(z^2)^{m+1/2}} + \frac{e^{-z^2}}{\pi} R_n, \quad (13)$$

restricting oneself by the first three items:

$$\exp(z_m^2) [1 - \operatorname{erf}(z_m)] \simeq \pi^{-1/2} \left\{ \frac{1}{z} - \frac{2}{2z^3} + \frac{3}{4z^5} - \dots \right\}.$$

Let us also use

$$\frac{1}{a+b} \left( \frac{1}{a^n} + \frac{1}{b^n} \right) = \frac{1}{ab} (a^{n-1} - a^{n-2}b + \dots - ab^{n-2} + b^{n-1}) \quad (14)$$

(at  $n=2m+1$ ). Now the relationship between absorption and REP for the homogeneous spectra Eq. (7) transforms into

$$I(\omega_0) \sim \xi^2 \left\{ |\tilde{\Phi}(\omega_0) - \tilde{\Phi}(\omega_0 - \omega)|^2 + \Delta^2 \left| \frac{d}{d\omega_0} (\tilde{\Phi}(\omega_0) - \tilde{\Phi}(\omega_0 - \omega)) \right|^2 + \frac{\Delta^4}{2} \left| \frac{d^2}{d\omega_0^2} (\tilde{\Phi}(\omega_0) - \tilde{\Phi}(\omega_0 - \omega)) \right|^2 - \dots \right\}, \quad (15)$$

where the function  $\tilde{\Phi}(\omega)$  is determined by the recorded inhomogeneous absorption spectrum by using the Kramers-Kronig transformation according to Eq. (4). Eq. (15) generalizes the transform method for the inhomogeneous systems where the effects of the inhomogeneous broadening are not large<sup>\*\*\*</sup>. The main new effect that ensues is the narrowing of REP. Therefore, if the experimental REPs are narrower than those calculated by the basic transform relationship Eq. (7), the reason can be the inhomogeneity of the medium. Eq. (15) allows also the estimation of the value of the inhomogeneous broadening.

<sup>\*\*\*</sup> An analogous relationship was obtained in [14] with the difference that instead of the inhomogeneous absorption spectra there was homogeneous absorption in the correction terms. This result is not correct.

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**TRANSFORMSEOS NEELDUMISE JA RESONANTSE KOMBINATSIOONHAJUMISE VAHEL MITTEHOMOGEENSETES KESKKONDADES**

Transformseos neeldumisspektri ja resonantse kombinatsioonhajumise ergastusspektri vahel on üldistatud juhule, kui molekulid (lisanditsentrid) asuvad mittehomo-geenses keskkonnas. Tuletatud valem kehtib üksnes siis, kui mittehomo-geenne laiene- mine on väiksem homogeensest.

Имби ТЕХВЕР

**СООТНОШЕНИЕ ПРЕОБРАЗОВАНИЯ МЕЖДУ ПОГЛОЩЕНИЕМ И РЕЗОНАНСНЫМ КОМБИНАЦИОННЫМ РАССЕЯНИЕМ В НЕОДНОРОДНЫХ СРЕДАХ**

Соотношение преобразования между спектром поглощения и спектром возбужде- ния резонансного комбинационного рассеяния, полученное ранее для ансамбля иден- тичных молекул, обобщено для молекул в неоднородной среде.

$$I_{\text{res}}(\omega) = \frac{\pi}{2\Delta} \sum_{\alpha} |C_{\alpha}|^2 \delta(\omega - \omega_{\alpha}) \quad (11)$$

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$$R_{\alpha} = \frac{1}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{1}{2n+1} \frac{d^{2n+1} \epsilon(\omega)}{d\omega^{2n+1}} \quad (12)$$

restricted oneself by the first three terms:  

$$\exp(\epsilon''(\omega)) [1 - \epsilon''(\omega)] \approx \epsilon''(\omega) \left( 1 - \frac{2}{2\epsilon''(\omega)} + \frac{3}{4\epsilon''(\omega)^2} - \dots \right)$$