

6.1. Time-Correlation Function Description of Absorption Lineshape

The interaction of light and matter as we have described from Fermi's Golden Rule gives the rates of transitions between discrete eigenstates of the material Hamiltonian H_0 . The frequency dependence to the transition rate is proportional to an absorption spectrum. We also know that interaction with the light field prepares superpositions of the eigenstates of H_0 , and this leads to the periodic oscillation of amplitude between the states. Nonetheless, the transition rate expression really seems to hide any time-dependent description of motions in the system. An alternative approach to spectroscopy is to recognize that the features in a spectrum are just a frequency domain representation of the underlying molecular dynamics of molecules. For absorption, the spectrum encodes the time-dependent changes of the molecular dipole moment for the system, which in turn depends on the position of electrons and nuclei.

A time-correlation function for the dipole operator can be used to describe the dynamics of an equilibrium ensemble that dictate an absorption spectrum. We will make use of the transition rate expressions from first-order perturbation theory that we derived in the previous section to express the absorption of radiation by dipoles as a correlation function in the dipole operator. Let's start with the rate of absorption and stimulated emission between an initial state $|\ell\rangle$ and final state $|k\rangle$ induced by a monochromatic field

$$w_{k\ell} = \frac{\pi E_0^2}{2\hbar^2} \left| \langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right] \quad (6.1)$$

We would like to use this to calculate the experimentally observable absorption coefficient (cross-section) which describes the transmission through the sample

$$T = \exp[-\Delta N \alpha(\omega) L]. \quad (6.2)$$

The absorption cross section describes the rate of energy absorption per unit time relative to the intensity of light incident on the sample

$$\alpha = \frac{\dot{E}_{rad}}{I}. \quad (6.3)$$

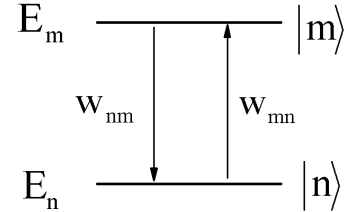
The incident intensity is

$$I = \frac{c}{8\pi} E_0^2. \quad (6.4)$$

If we have two discrete states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$, the rate of energy absorption is proportional to the absorption rate and the transition energy

$$\dot{E}_{rad} = w_{nm} \cdot \hbar \omega_{nm}. \quad (6.5)$$

For an ensemble this rate must be scaled by the probability of occupying the initial state. More generally, we want to consider the rate of energy loss from the field as a result of the difference in rates of absorption and stimulated emission between states populated with a thermal distribution. So, summing all possible initial and final states $|\ell\rangle$ and $|k\rangle$ over all possible upper and lower states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$



$$\begin{aligned} \dot{E}_{rad} &= \sum_{\ell, k=m, n} p_{\ell} w_{k\ell} \hbar \omega_{k\ell} \\ &= \frac{\pi E_0^2}{2\hbar} \sum_{\ell, k=m, n} \omega_{k\ell} p_{\ell} \left| \langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]. \end{aligned} \quad (6.6)$$

The cross section including absorption $|n\rangle \rightarrow |m\rangle$ and stimulated emission $|m\rangle \rightarrow |n\rangle$ terms is:

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \sum_{n, m} \left[\omega_{mn} p_n \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega) + \omega_{nm} p_m \left| \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \right|^2 \delta(\omega_{nm} + \omega) \right] \quad (6.7)$$

To simplify this we note:

- 1) Since $\delta(x) = \delta(-x)$, $\delta(\omega_{nm} + \omega) = \delta(-\omega_{nm} + \omega) = \delta(\omega_{mn} - \omega)$.
- 2) The matrix elements squared in the two terms are the same: $\left| \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \right|^2 = \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2$ For shorthand we will write $|\bar{\mu}_{mn}|^2$
- 3) $\omega_{mn} = -\omega_{nm}$.

So,

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \sum_{n, m} \omega_{mn} (p_n - p_m) |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) \quad (6.8)$$

Here we see that the absorption coefficient depends on the population difference between the two states. This is expected since absorption will lead to loss of intensity, whereas stimulated emission

leads to gain. With equal populations in the upper and lower state, no change to the incident field would be expected. Since $p_\ell = \exp[-\beta E_\ell] / Z$

$$p_n - p_m = p_n (1 - \exp[-\beta \hbar \omega_{nm}]) \quad (6.9)$$

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sum_{n,m} p_n |\bar{\mu}_{nm}|^2 \delta(\omega_{nm} - \omega) \quad (6.10)$$

Note, that the two ω_{nm} factors in eq. (6.8) have just been replaced with ω because the delta function enforces this equality. We can now separate α into a product of factors that represent the field, and the matter, where the matter is described by $\sigma(\omega)$, the absorption lineshape.

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sigma(\omega) \quad (6.11)$$

$$\sigma(\omega) = \sum_{n,m} p_n |\bar{\mu}_{nm}|^2 \delta(\omega_{nm} - \omega) \quad (6.12)$$

We have already indicated that expressions of the form (6.12) can be expressed as a correlation function in the operator μ , so following our earlier derivation,

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon} \cdot \bar{\mu}_I(0) \hat{\epsilon} \cdot \bar{\mu}_I(t) \rangle \quad (6.13)$$

Here, I added back the light field polarization for a moment. If you assume an isotropic light field, then you can show that (6.13) can be written as

$$\sigma(\omega) = \frac{1}{2\pi} \cdot \frac{1}{3} \cdot \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\mu}_I(0) \bar{\mu}_I(t) \rangle \quad (6.14)$$

or

$$\sigma(\omega) = \frac{1}{6\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \bar{\mu}_I(t) \bar{\mu}_I(0) \rangle \quad (6.15)$$

The absorption lineshape is given by the Fourier transform of the dipole correlation function. The correlation function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of E field and contains information on states of system and broadening due to relaxation.

6.2. Examples

So the absorption spectrum in any frequency region is given by the Fourier transform over the dipole correlation function that describes the time-evolving charge distributions in molecules, solids, and nanosystems. Let's consider how this manifests itself in a few different spectroscopies, which have different contributions to the dipole operator. In general the dipole operator is a relatively simple representation of the charged particles of the system:

$$\bar{\mu} = \sum_i q_i (\bar{r}_i - \bar{r}_0). \quad (6.16)$$

The complexity arises from the time-dependence of this operator, which evolves under the full Hamiltonian for the system:

$$\bar{\mu}(t) = e^{iH_0 t} \bar{\mu}(0) e^{-iH_0 t} \quad (6.17)$$

$$H_0 = H_{elec} + H_{vib} + H_{rot} + H_{spin} + \dots + H_{bath} + \dots \quad (6.18)$$

The full Hamiltonian accounts for the dynamics of all electronic, nuclear, and spin degrees of freedom. It is expressed in eq. (6.18) in terms of separable contributions from those degrees of freedom and a bath Hamiltonian that contains all of the dark degrees of freedom not explicitly included in the dipole operator. (For now, I've left out terms such as $H_{elec-vib}$ and $H_{vib-rot}$ that involve pairwise couplings between different degrees of freedom). If we are fortunate enough to write the Hamiltonian in this form, then the wavefunction for the system can be written as product states of the wavefunctions for the different degrees of freedom,

$$|\psi\rangle = |\psi_{elec} \psi_{vib} \psi_{rot} \dots \psi_{bath}\rangle \quad (6.19)$$

and the correlation function can be separated into a product of correlation functions from various sources:

$$C_{\mu\mu}(t) = C_{elec}(t) C_{vib}(t) C_{rot}(t) \dots \quad (6.20)$$

$$C_{vib}(t) = \sum_{n(vib)} p_n \langle \psi_{vib,n} | e^{iH_{vib} t} \mu e^{-iH_{vib} t} \mu | \psi_{vib,n} \rangle \quad (6.21)$$

The net correlation function will have oscillatory components at many frequencies and its Fourier transform will give the full absorption spectrum from the ultraviolet to the microwave regions of the spectrum. Generally speaking the highest frequency contributions (electronic or UV/Vis) will be modulated by contributions from lower frequency motions (...such as vibrations and rotations). However, we can separately analyze each of these contributions to the spectrum.

Atomic transitions

$H_0 = H_{atom}$. For hydrogenic orbitals, $|n\rangle \rightarrow |n \ell m_\ell\rangle$.

Rotational spectroscopy

From a classical perspective, the dipole moment can be written in terms of a permanent dipole moment with amplitude and direction

$$\bar{\mu} = \mu_0 \hat{u} \quad (6.22)$$

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \mu_0^2 \langle \hat{\varepsilon} \cdot \hat{u}(0) \hat{\varepsilon} \cdot \hat{u}(t) \rangle \quad (6.23)$$

The lineshape is the Fourier transform of the rotational motion of the permanent dipole vector in the laboratory frame. The frequency of the resonance would depend on the rate of rotation – the angular momentum and the moment of inertia. Collisions or other damping would lead to the broadening of the lines.

Quantum mechanically we expect a series of rotational resonances that mirror the thermal occupation and degeneracy of rotational states for the system. Taking a case with cylindrical symmetry as an example, the Hamiltonian is

$$H_{rot} = \frac{\bar{L}^2}{2I} \quad (6.24)$$

and the wavefunctions are spherical harmonics are described by

$$\begin{aligned} \bar{L}^2 |Y_{J,M}\rangle &= \hbar^2 J(J+1) |Y_{J,M}\rangle \\ L_Z |Y_{J,M}\rangle &= M\hbar |Y_{J,M}\rangle \end{aligned} \quad (6.25)$$

If we take a dipole operator in the form of eq. (6.22), then the far-infrared rotational spectrum will be described by the correlation function

$$C_{rot}(t) = \sum_{J,M} p_{J,M} |\mu_0|^2 \langle Y_{J,M} | e^{iH_{rot}t} (\hat{u} \cdot \hat{\varepsilon}) e^{-iH_{rot}t} (\hat{u} \cdot \hat{\varepsilon}) | Y_{J,M} \rangle. \quad (6.26)$$

Here the evaluation of this correlation function involves an orientational average. For instance, the matrix element

$$\langle Y_{J',M'} | (\hat{u} \cdot \hat{\varepsilon}_Z) | Y_{J,M} \rangle = \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta Y_{J',M'}^* \cos\theta Y_{J,M}. \quad (6.27)$$

These functions are readily evaluated using reduction formulas such as

$$\cos\theta |Y_{J,M}\rangle = c_+ |Y_{J+1,M}\rangle + c_- |Y_{J-1,M}\rangle \quad (6.28)$$

$$c_+ = \sqrt{\frac{(J+1)^2 - M^2}{4(J+1)^2 - 1}} \quad c_- = \sqrt{\frac{J^2 + M^2}{4J^2 - 1}} \quad (6.29)$$

and the orthogonality of spherical harmonics

$$\langle Y_{J',M'} | Y_{J,M} \rangle = 4\pi \delta_{J',J} \delta_{M',M}. \quad (6.30)$$

These expressions in eq. (6.26) lead to the correlation function

$$C_{rot}(t) = \frac{1}{Z_{rot}} \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)} \left[e^{-i(J+1)2\bar{B}t} + e^{iJ2\bar{B}t} \right] \quad (6.31)$$

where the rotational constant is

$$\bar{B} = \frac{\hbar}{4\pi I c}. \quad (6.32)$$

Fourier transforming eq. (6.31) leads to the lineshape

$$\sigma_{rot}(\omega) = \frac{1}{2\pi Z_{rot}} \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)} \left[\delta(\omega - i2\bar{B}(J+1)) + \delta(\omega + i2\bar{B}J) \right]. \quad (6.33)$$

The two terms reflect the fact that each thermally populated level with $J > 0$ contributes both to absorptive and stimulated emission processes, and the observed intensity reflects the difference in populations.

IR Vibrational Spectroscopy

Vibrational spectroscopy can be described by taking the dipole moment to be weakly dependent on the displacement of vibrational coordinates q

$$\bar{\mu} = \bar{\mu}_0 + \left. \frac{\partial \bar{\mu}}{\partial q} \right|_{q=q_0} q + \dots \quad (6.34)$$

Here the first expansion term is the permanent dipole moment and the second term is the transition dipole moment. If we are performing our ensemble average over vibrational states, the lineshape becomes the Fourier transform of a correlation function in the vibrational coordinate

$$\sigma(\omega) = \frac{1}{2\pi} \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle q(0)q(t) \rangle \quad (6.35)$$

The vector nature of the transition dipole has been dropped here. So the time-dependent dynamics of the vibrational coordinate dictate the IR lineshape.

This approach holds for the classical and quantum mechanical cases. In the case of quantum mechanics, the change in charge distribution in the transition dipole moment is replaced with the equivalent transition dipole matrix element. If we take the vibrational Hamiltonian to be that of a harmonic oscillator,

$$H_{vib} = \frac{1}{2m} p^2 + \frac{1}{2} m \omega_0^2 q^2 = \hbar \omega_0 \left(a^\dagger a + \frac{1}{2} \right), \quad (6.36)$$

then the time-dependence of the vibrational coordinate, expressed as raising and lowering operators is

$$q(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \left(a^\dagger e^{i\omega_0 t} + a e^{-i\omega_0 t} \right). \quad (6.37)$$

The absorption lineshape is then obtained from eq. (6.35).

$$\sigma_{vib}(\omega) = \frac{1}{2\pi} \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \frac{1}{Z_{vib}} \sum_n e^{-\beta n \hbar \omega_0} \left[\delta(\omega - n\omega_0) + \delta(\omega + n\omega_0) \right] \quad (6.38)$$

or for the low temperature limit applicable to most vibrations at room temperature:

$$\sigma_{vib}(\omega) = \frac{1}{2\pi} \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \delta(\omega - \omega_0). \quad (6.39)$$

Raman Spectroscopy

Technically, we need second-order perturbation theory to describe Raman scattering, because transitions between two states are induced by the action of two light fields whose frequency difference equals the energy splitting between states. But much the same result is obtained if we replace the dipole operator with an induced dipole moment generated by the incident field: $\bar{\mu} \Rightarrow \bar{\mu}_{ind}$. The incident field E_i polarizes the molecule,

$$\bar{\mu}_{ind} = \bar{\alpha} \cdot \bar{E}_i(t). \quad (6.40)$$

($\bar{\alpha}$ is the polarizability), and the scattered light field results from the interaction with this induced dipole

$$\begin{aligned} V(t) &= -\bar{\mu}_{ind} \cdot \bar{E}_s(t) \\ &= \bar{E}_s(t) \cdot \bar{\alpha} \cdot \bar{E}_i(t) \\ &= E_s(t) E_i(t) (\hat{\epsilon}_s \cdot \bar{\alpha} \cdot \hat{\epsilon}_i) \end{aligned} \quad (6.41)$$

Here we have written the polarization components of the incident (i) and scattered (s) light projecting onto the polarizability tensor $\bar{\bar{\alpha}}$. Equation (6.41) leads to an expression for the Raman lineshape as

$$\begin{aligned}\sigma(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon}_s \cdot \bar{\bar{\alpha}}(0) \cdot \hat{\epsilon}_i \hat{\epsilon}_s \cdot \bar{\bar{\alpha}}(t) \cdot \hat{\epsilon}_i \rangle \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\bar{\alpha}}(0) \bar{\bar{\alpha}}(t) \rangle\end{aligned}\quad (6.42)$$

To evaluate this, the polarizability tensor can also be expanded in the nuclear coordinates

$$\bar{\bar{\alpha}} = \bar{\bar{\alpha}}_0 + \left. \frac{\partial \bar{\bar{\alpha}}}{\partial q} \right|_{q=q_0} q + \dots \quad (6.43)$$

where the leading term would lead to Rayleigh scattering and rotational Raman spectra, and the second term would give vibrational Raman scattering.

Also remember that the polarizability tensor is a second rank tensor that tells you how well a light field polarized along i can induce a dipole moment (light-field-induced charge displacement) in the s direction. For cylindrically symmetric systems which have a polarizability component α_{\parallel} along the principal axis of the molecule and a component α_{\perp} perpendicular to that axis, this usually takes the form

$$\bar{\bar{\alpha}} = \begin{pmatrix} \alpha_{\parallel} & & \\ & \alpha_{\perp} & \\ & & \alpha_{\perp} \end{pmatrix} = \alpha \mathbf{I} + \frac{1}{3} \beta \begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \quad (6.44)$$

where α is the isotropic component of polarizability tensor and β is the anisotropic component.

6.3. Ensemble Averaging and Line-Broadening

We have seen that an absorption lineshape can represent the dynamics of the dipole or be broadened by energy relaxation (i.e., coupling to continuum). However, there are numerous processes that can influence the lineshape. These can be broken into intrinsically molecular and ensemble average effects. These can be further separated by dynamic processes (homogeneous broadening) and static effects (inhomogeneous broadening). Let's review the phenomenological description. The separation of these effects is a

1. Homogeneous broadening

Several homogeneous (dynamic) line broadening mechanisms are possible, which are qualitatively captured by a time-scale T_2 . If these processes are independent, the exponential rates for different contributions add:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{\tau_{or}} \quad (6.45)$$

a. Molecular processes

Population Relaxation. Population relaxation T_1 refers to amplitude decay in the coherent superposition created by the light field as a result of its finite lifetime. This can have contributions from radiative decay (spontaneous emission processes) or non-radiative processes (i.e., coupling to continuum and IVR)

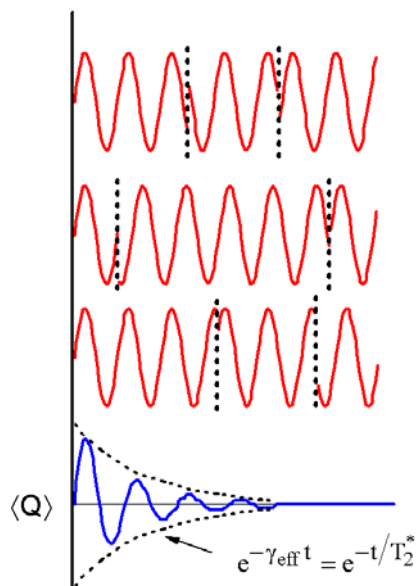
$$\frac{1}{T_1} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}} \quad (6.46)$$

In this case, ensemble averaging doesn't change the measurement. All members of ensemble behave identically and the experimentally measured decay is the microscopic lifetime.

The observed population relaxation time depends on both the relaxation times of the upper and lower states (m and n) being coupled by the field: $1/T_1 = w_{mn} + w_{nm}$. When the energy splitting is high, only the downward rate contributes, which is why the rate is often written $1/2T_1$.

b. Ensemble processes

Pure Dephasing. Pure dephasing is characterized by a time constant T_2^* that characterizes the randomization of phase within an ensemble as a result of molecular interactions. This is a dynamic ensemble averaging effect in which the phase relationship of oscillation between members of the ensemble is gradually destroyed. Examples include collisions in a dense gas, or fluctuations induced by a solvent.

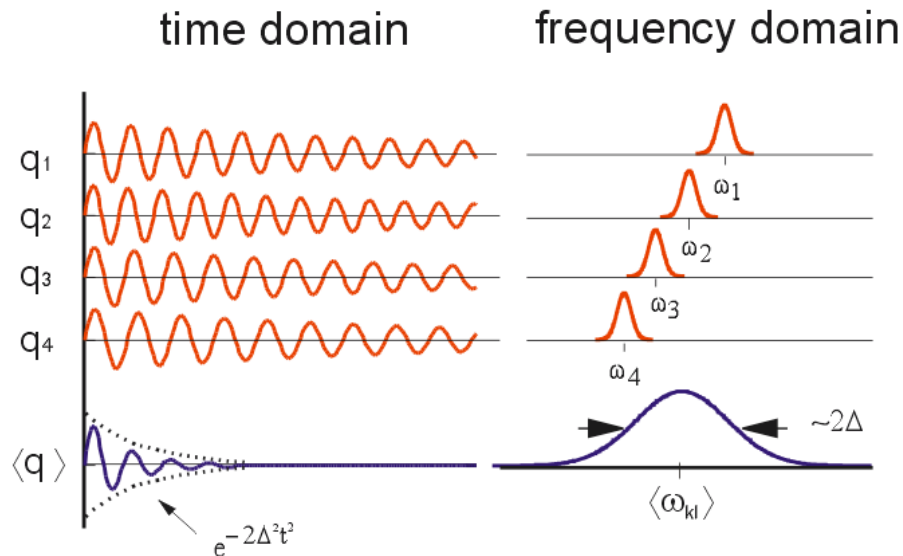


Orientational relaxation (τ_{or}) also leads to relaxation of the dipole correlation function and to line broadening. Since the correlation function depends on the projection of the dipole onto a fixed axis in the laboratory frame, randomization of the initial dipole orientations is an ensemble averaged dephasing effect. In solution, this process is commonly treated as an orientational diffusion problem in which τ_{or} is proportional to the diffusion constant.

2. Inhomogeneous Broadening

Absorption lineshapes can also be broadened by a static distribution of frequencies. If molecules within the ensemble are influenced static environmental variations more than other processes, then the observed lineshape reports on the distribution of environments. This inhomogeneous

broadening is a static ensemble averaging effect, which hides the dynamical content in the homogeneous linewidth. The origin of the inhomogeneous broadening can be molecular (for instance a distribution of defects in crystals) or macroscopic (i.e. an inhomogeneous magnetic field in NMR).



The inhomogeneous linewidth is dictated the width of the distribution Δ .

Total Linewidth

The total observed broadening of the absorption lineshape reflects the contribution of all of these effects:

$$\langle \mu(0)\mu(t) \rangle \propto \exp \left[-t \left(\frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{\tau_{or}} \right) \right] e^{-\Delta^2 t^2 / 2} \quad (6.47)$$

These effects can be wrapped into a lineshape function $g(t)$. The lineshape for the broadening of a given transition can be written as the Fourier transform over the oscillating transition frequency damped and modulated by a complex $g(t)$:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} e^{i\omega_{mn}t - g(t)} \quad (6.48)$$

All of these effects can be present simultaneously in an absorption spectrum.