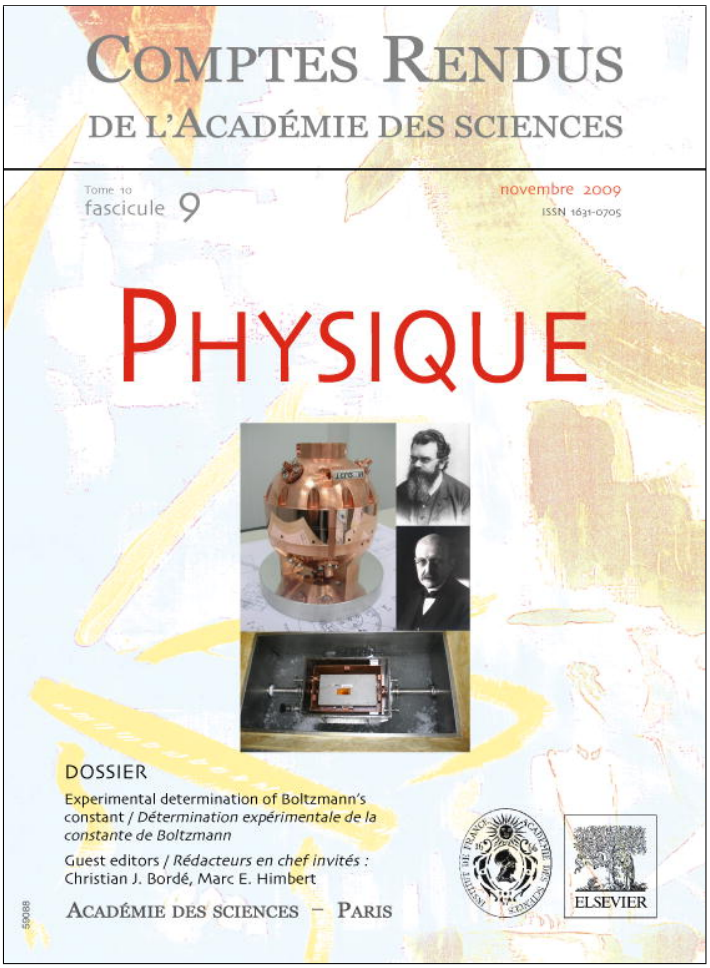

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C. R. Physique 10 (2009) 866–882
COMPTES RENDUS PHYSIQUE

Experimental determination of Boltzmann's constant

On the theory of linear absorption line shapes in gases

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Available online 24 November 2009

Abstract

A detailed theory of the line shape in linear absorption spectroscopy of low-pressure gases is developed. The goal is to take into account all effects that come into play in the determination of Boltzmann's constant from measurements of the Doppler width. We demonstrate that there is no additional broadening from finite transit time across the laser beams. The molecular recoil and the second-order Doppler effect are included in the line shape thanks to a complete quantum treatment. The Mössbauer–Lamb–Dicke narrowing of Doppler lines by collisions is also included and the special cases of Galatry and Nelkin–Ghatak profiles are presented. ***To cite this article: C.J. Bordé, C. R. Physique 10 (2009).***

Résumé

Sur la théorie de la forme des raies d'absorption linéaire des gaz. Une théorie détaillée de la forme des raies d'absorption linéaire des gaz à basse pression est développée. L'objectif est de mieux cerner tous les effets susceptibles d'intervenir dans la détermination de la constante de Boltzmann à partir d'une mesure de la largeur Doppler. On démontre en particulier qu'il n'y a pas d'élargissement supplémentaire lié au temps fini de traversée du faisceau laser par les molécules. Les effets de recul et Doppler du deuxième ordre sont intégrés dans la forme de raie grâce à un traitement quantique complet. L'effet Mössbauer–Lamb–Dicke de rétrécissement des raies Doppler par les collisions est lui aussi incorporé dans la théorie avec comme cas particuliers les profils de Galatry et de Nelkin–Ghatak. ***Pour citer cet article : C.J. Bordé, C. R. Physique 10 (2009).***

Keywords: Absorption line shape; Laser spectroscopy; Doppler width; Transit-time broadening; Boltzmann constant; Base units of the SI

Mots-clés : Forme de raie d'absorption ; Spectroscopie laser ; Largeur Doppler ; Élargissement dû au transit ; Constante de Boltzmann ; Unités de base du SI

1. Introduction

Several experiments are presently underway to determine Boltzmann constant from the Doppler width of an absorption line in an atomic or in a molecular gas. Three of these are presented in this volume [1–3] but at least three others are in preparation. This possibility was suggested by the author on the occasion of the 125th anniversary of the meter convention [4–9]. In order to extract this Doppler width from the absorption profile, a detailed knowledge of the

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1631-0705/$ – see front matter
doi:10.1016/j.crhy.2009.10.019

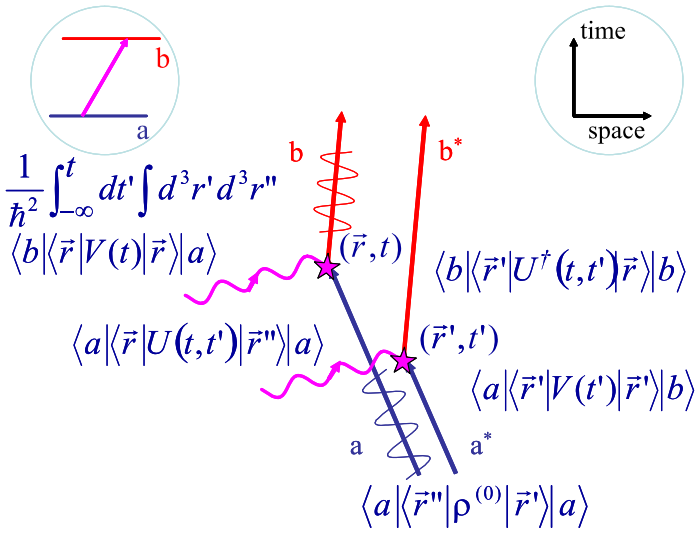

Fig. 1. Interferometric representation of the linear absorption process. This is one out of four different diagrams and their complex conjugates [11] representing the various terms of Eq. (4).

line shape is required which includes a number of small effects coming into play at a 10^{-6} level of accuracy. A key issue was the possible occurrence of transit effects owing to the transverse structure of the laser beams. It is shown in this article that this is not the case in linear absorption spectroscopy provided that the medium is uniform and isotropic. Other effects that are considered are the recoil effect and the second-order Doppler shift. We start with the traditional classical motion approach of molecules flying across the laser beams. The absence of transit effects is better understood in a plane wave approach. For a more rigorous theory of the molecular recoil, we quantize the molecular motion. The connection with the theory of neutron diffusion and gamma-ray spectroscopy is then presented and in this context the Brownian motion of molecules can be included through Van Hove's self-correlation function G_s. This leads to the well-known Galatry profile, which is one way to introduce the Mössbauer–Lamb–Dicke (MLD) narrowing. Finally, the complete theory in which momentum-changing collisions are introduced through collision kernels in the density matrix equations is outlined and confirms the absence of transit broadening in usual conditions. As an example the Nelkin–Ghatak profile is also derived as another way to describe the MLD narrowing. We start from the most basic level with Schrödinger equation for a two-level atomic system interacting with laser light and derive a very general expression for the gas absorbance.

2. Transition probability and absorbed luminous power in effective two-level atomic systems

2.1. Density operator evolution and associated diagram [10]

Let us consider a two-level system (Fig. 1) with internal state ket vectors $|a\rangle$, $|b\rangle$ (with $E_a < E_b$) interacting with a radiation field through the effective Hamiltonian $V(t)$. In a first approach, we shall consider that the evolution of the density operator $\rho(t)$ is the same as in the pure case $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$ where the state vectors $|\psi(t)\rangle$ satisfy Schrödinger equation:

$$i\hbar\partial_t\big|\psi(t)\big\rangle = \big(H + V(t)\big)\big|\psi(t)\big\rangle \tag{1}$$

except for a simple relaxation term[1] towards a time-independent equilibrium density operator $\rho^{(0)}$

$$i\hbar\frac{\partial\rho(t)}{\partial t} = \big[H + V(t), \rho(t)\big] - \frac{i\hbar}{2}\big\{\Gamma, \rho(t) - \rho^{(0)}\big\} \tag{2}$$

[1] Strictly speaking any relaxation model involves a trace operation over an external reservoir and the two-level system has no longer a wave function but must be described by a reduced density operator. However as long as we stick to a simple relaxation constant for each level it is convenient and mathematically correct to continue to keep a pure case description in terms of a state vector.

with standard notations: [,] for commutators and { , } for anticommutators. The unperturbed Hamiltonian H includes both the internal Hamiltonian operator and the kinetic energy operator. The relaxation operator Γ has eigenvalues γ_a and γ_b and we shall use the traditional notation $\gamma_{ba} = \gamma_{ab} = (\gamma_a + \gamma_b)/2$ for the relaxation constant of the optical dipole.

The integral form of the equation for $\rho(t)$ is:

$$\rho(t) = \rho^{(0)} + \frac{1}{i\hbar}\int_{-\infty}^{t} \mathrm{d}t'\, U\big(t,t'\big)\big[V\big(t'\big),\rho\big(t'\big)\big]U^{\dagger}\big(t,t'\big) \tag{3}$$

where the free evolution operator $U(t,t')$ satisfies $i\hbar\partial_t U(t,t') = (H - i\hbar\Gamma/2)U(t,t')$ with $U(t,t) = I$. Combining the two previous equations for the density operator $\rho(t)$, we obtain its rate of change under the influence of the radiation:

$$\left[\frac{\partial\rho(t)}{\partial t}\right]_{\text{interaction}} = \frac{1}{i\hbar}\big[V(t),\rho^{(0)}\big] - \frac{1}{\hbar^2}\int_{-\infty}^{t}\mathrm{d}t'\,\big[V(t),U\big(t,t'\big)\big[V\big(t'\big),\rho\big(t'\big)\big]U^{\dagger}\big(t,t'\big)\big] \tag{4}$$

We shall assume that $\rho^{(0)}$ is diagonal in the internal state basis. To second-order in V, the rate of formation of the excited state from the lower state under the influence of the radiation is obtained from the previous equation by introducing closure relations and keeping only the two relevant conjugate terms among eight possible ones:

$$\begin{aligned}\left[\frac{\partial\rho^{(2)}_{bb}(\vec{r},t)}{\partial t}\right]_{\text{interaction}} &= \hbar^{-2}V_{ba}(\vec{r},t)\int_{-\infty}^{t}\mathrm{d}t'\int\mathrm{d}^3r'\,\mathrm{d}^3r''\langle a|\langle\vec{r}|U\big(t,t'\big)\big|\vec{r}''\big\rangle|a\rangle\langle a|\big\langle\vec{r}''\big|\rho^{(0)}\big|\vec{r}'\big\rangle|a\rangle\\ &\quad\times V_{ab}\big(\vec{r}',t'\big)\langle b|\big\langle\vec{r}'\big|U^{\dagger}\big(t,t'\big)|\vec{r}\rangle|b\rangle + \text{c.c.}\end{aligned} \tag{5}$$

with $V_{ba}(\vec{r},t) = \langle b|\langle\vec{r}|V(t)|\vec{r}\rangle|a\rangle = V^*_{ab}(\vec{r},t)$. This equation is represented by a density matrix diagram (see Fig. 1). The source term is the atomic coherence (in the atom optics sense): $\langle a|\langle\vec{r}''|\rho^{(0)}|\vec{r}'\rangle|a\rangle$. The matrix elements $\langle a|\langle\vec{r}|U(t,t')|\vec{r}''\rangle|a\rangle$ and $\langle b|\langle\vec{r}|U(t,t')|\vec{r}'\rangle|b\rangle$ are the propagators of states a and b:

$$\langle a|\langle\vec{r}|U\big(t,t'\big)\big|\vec{r}'\big\rangle|a\rangle = K_a\big(\vec{r},\vec{r}',t-t'\big)\exp\big(-\gamma_a\big|t-t'\big|/2\big) \tag{6}$$

with

$$K_a\big(\vec{r},\vec{r}',t-t'\big) = \langle a|\langle\vec{r}|\exp\big[-iH\big(t-t'\big)/\hbar\big]\big|\vec{r}'\big\rangle|a\rangle \tag{7}$$

and similarly

$$\langle b|\big\langle\vec{r}'\big|U^{\dagger}\big(t,t'\big)|\vec{r}\rangle|b\rangle = K^*_b\big(\vec{r},\vec{r}',t-t'\big)\exp\big(-\gamma_b\big|t-t'\big|/2\big) \tag{8}$$

In the following we shall assume the usual canonical ensemble of states with a constant number of molecules N. The thermal equilibrium density operator $\rho^{(0)}$ satisfies the Bloch equation:

$$\frac{\partial\rho^{(0)}}{\partial\beta} = -\frac{1}{2}\big\{H - \langle E\rangle,\rho^{(0)}\big\} \tag{9}$$

with $\beta = 1/k_{\mathrm{B}}T$ and average energy

$$\langle E\rangle = \frac{\mathrm{Tr}[H\exp[-\beta H]]}{\mathrm{Tr}\exp[-\beta H]} = -\frac{\partial\ln Z}{\partial\beta} \tag{10}$$

where Z is the total partition function (internal and external):

$$Z = \mathrm{Tr}\exp[-\beta H] = Z_{\text{int}}Z_{\text{ext}} \tag{11}$$

The Hamiltonian H is the same as in Schrödinger (1) and Liouville–von Neumann (2) equations. Thus the equilibrium density operator is given by

$$\rho^{(0)} = (N/Z)\exp[-H\beta] \tag{12}$$

and is normalized so that its trace is the total (constant) number of molecules in the volume V:

$$\operatorname{Tr}\rho^{(0)} = N \tag{13}$$

and the number of molecules per unit volume will be written

$$n^{(0)} = N/V \tag{14}$$

The atomic coherence is Gaussian:

$$\begin{aligned}\langle a|\langle\vec{r}|\rho^{(0)}|\vec{r}'\rangle|a\rangle &= (N/Z)\int \mathrm{d}^3p\,\mathrm{d}^3p'\,\langle\vec{r}|\vec{p}\rangle\langle a|\langle\vec{p}|\exp[-\beta H]|\vec{p}'\rangle|a\rangle\langle\vec{p}'|\vec{r}'\rangle \\ &= (N/Z)\exp(-E_a\beta)\frac{1}{\lambda_T^3}\exp\bigl[-\pi\bigl(\vec{r}-\vec{r}'\bigr)^2/\lambda_T^2\bigr]\end{aligned} \tag{15}$$

and its width is equal to the thermal de Broglie wavelength

$$\lambda_T = \frac{h}{\sqrt{\pi}Mu} \tag{16}$$

corresponding to the molecular mass M and to the most probable velocity u at temperature T:

$$u = \sqrt{\frac{2k_{\mathrm{B}}T}{M}} = \sqrt{\frac{2}{M\beta}} \tag{17}$$

so that

$$Z_{\mathrm{ext}} = V/\lambda_T^3 \tag{18}$$

Linear absorption thus appears as an interferometric process [13] probing the thermal coherence of the gas. The visibility of the interference pattern is limited by the coherence length λ_T and the Doppler width $\Delta\nu_D$ (e-fold half-width) is the width of the central fringe of the interferogram

$$\Delta\nu_D/\nu = \lambda_C/(\sqrt{\pi}\,\lambda_T) \tag{19}$$

where $\lambda_C = h/Mc$ is the de Broglie–Compton wavelength of the molecules. Side fringes are wiped out by the averaging over the separation of the two interactions of Fig. 1. They would appear for spatially or temporally separated fields in a Ramsey configuration with a fixed separation.

2.2. Thermal propagator and absorbed power

A simplification occurs when the same Hamiltonian drives the time and temperature evolutions, since we may write:

$$\begin{aligned}\left[\frac{\partial\rho_{bb}^{(2)}(\vec{r},t)}{\partial t}\right]_{\substack{\mathrm{inter}\\ \mathrm{action}}} &= \hbar^{-2}V_{ba}(\vec{r},t)\int_{-\infty}^{t}\mathrm{d}t'\int\mathrm{d}^3r'\bigl\{\langle a|\langle\vec{r}|U\bigl(t,t'\bigr)\rho^{(0)}|\vec{r}'\rangle|a\rangle \\ &\quad\times V_{ab}\bigl(\vec{r}',t'\bigr)\langle b|\bigl\langle\vec{r}'\bigr|U^{\dagger}\bigl(t,t'\bigr)|\vec{r}\rangle|b\rangle\bigr\} + \mathrm{c.c.}\end{aligned} \tag{20}$$

where:

$$\begin{aligned}\langle a|\langle\vec{r}|U\bigl(t,t'\bigr)\rho^{(0)}|\vec{r}'\rangle|a\rangle &= (N/Z)\langle a|\langle\vec{r}|\exp\bigl[-iH\bigl(t-t'-i\hbar\beta\bigr)/\hbar\bigr]|\vec{r}'\rangle|a\rangle\exp\bigl(-\gamma_a\bigl|t-t'\bigr|/2\bigr) \\ &= (N/Z)K_a\bigl(\vec{r},\vec{r}',t-t'-i\hbar\beta\bigr)\exp\bigl(-\gamma_a\bigl|t-t'\bigr|/2\bigr)\end{aligned} \tag{21}$$

The product $K_a(\vec{r},\vec{r}',\tau-i\hbar\beta)K_b^*(\vec{r},\vec{r}',\tau)\exp(-\gamma_{ba}|t-t'|)$ is the thermal propagator of the off-diagonal density matrix element (optical coherence in the atomic physics sense).

For one-photon transitions in a two-level system, the matrix element of the Hamiltonian of interaction with a monochromatic electromagnetic wave of circular frequency $\omega = 2\pi\nu$ is

$$V_{ba}(\vec{r},t) = -\hbar\Omega_{ba} e^{i(\omega t+\varphi)} U(\vec{r}) + \text{c.c.} \tag{22}$$

where Ω_{ba} is a Rabi frequency $\mu_{ba} E_0/2\hbar$ and where:

$$U(\vec{r}) = e^{-ik(z-z_0)} U_0(\vec{r}) \tag{23}$$

is the geometrical dependence of the light beam propagating forward in the z direction. If the absorbing gas is optically thick, we shall use a complex value for k in order to account for the exponential decrease of the wave amplitude:

$$k = k' - ik'' \tag{24}$$

where

$$2k'' = k_\nu = -\frac{1}{P_L(z)} \frac{\mathrm{d}P_L(z)}{\mathrm{d}z} \tag{25}$$

is the absorption coefficient for the laser power P_L:

$$P_L(z) = c\frac{\varepsilon_0 E_0^2(z)}{2} S \tag{26}$$

carried in the effective surface

$$S = \int \mathrm{d}x\, \mathrm{d}y\, U_0(\vec{r}) U_0^*(\vec{r}) \tag{27}$$

In the case of an absorption coefficient independent of z this leads to Bouguer–Lambert law over the length L of absorbing material:

$$P_L(z_0 + L) = P_L(z_0) \exp\bigl(-2k''L\bigr) \tag{28}$$

More generally we shall calculate the dimensionless absorbance (optical density or extinction):

$$A_\nu = \int_{z_0}^{z_0+L} k_\nu \,\mathrm{d}z = \ln \frac{P_L(z_0)}{P_L(z_0+L)} \tag{29}$$

From

$$\left[\frac{\partial \rho_{bb}^{(2)}(\vec{r},t)}{\partial t}\right]_{\substack{\text{inter}\\ \text{action}}} = \frac{n^{(0)}\lambda_T^3}{Z_{\text{int}}} \Omega_{ba}^2 e^{-2k''(z-z_0)} 2\,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega+\gamma_{ba})\tau} \times \int \mathrm{d}^3 r'\, U_0^*(\vec{r}) U_0\bigl(\vec{r}'\bigr) e^{-ik(z'-z)} K_a\bigl(\vec{r},\vec{r}',\tau - i\hbar\beta\bigr) K_b^*\bigl(\vec{r},\vec{r}',\tau\bigr) \tag{30}$$

we can express the absorbed power per unit length as:

$$\frac{\mathrm{d}\mathfrak{P}_{abs}}{\mathrm{d}z} = -\frac{\mathrm{d}P_L(z)}{\mathrm{d}z} = \hbar\omega \int \mathrm{d}x\, \mathrm{d}y \left[\frac{\partial \rho_{bb}^{(2)}(\vec{r},t)}{\partial t}\right]_{\substack{\text{inter}\\ \text{action}}}$$

and the absorption coefficient as:

$$k_\nu = 4\pi^2 \nu \alpha d_{ba}^2 \frac{n^{(0)}\lambda_T^3}{Z_{\text{int}}} 2\,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega+\gamma_{ba})\tau} \times \frac{1}{S} \int \mathrm{d}x\, \mathrm{d}y \int \mathrm{d}^3 r'\, U_0^*(\vec{r}) U_0\bigl(\vec{r}'\bigr) e^{-ik(z'-z)} K_a\bigl(\vec{r},\vec{r}',\tau - i\hbar\beta\bigr) K_b^*\bigl(\vec{r},\vec{r}',\tau\bigr) \tag{31}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c)$ is the fine structure constant and $d_{ba} = \mu_{ba}/e$. Finally, the dimensionless absorbance A_ν can be written

$$A_\nu = \int_{z_0}^{z_0+L} k_\nu \,\mathrm{d}z = 2\pi\alpha \frac{n^{(0)} d_{ba}^2 L}{Z_{\mathrm{int}}} 2\omega \,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega+\gamma_{ba})\tau} \times \frac{\lambda_T^3}{SL} \int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, U_0^*(\vec{r}) U_0(\vec{r}') e^{-ik(z'-z)} K_a\big(\vec{r},\vec{r}',\tau - i\hbar\beta\big) K_b^*\big(\vec{r},\vec{r}',\tau\big) \tag{32}$$

This is the quantity directly obtained from the measurement by taking the logarithm of the transmitted power as a function of the laser frequency. It is the product by 2π of the universal coupling constant α, of a spatial filling factor $\eta_{ba} = n^{(0)} d_{ba}^2 L$, of a thermal filling factor $e^{-E_a\beta}/Z_{\mathrm{int}}$, of a line quality factor $Q = \omega f(\omega_{ba})$ and of a normalized line shape $f(\omega - \omega_{ba})$ such that $\int_{-\infty}^{+\infty} f(\omega - \omega_{ba})\,\mathrm{d}\nu = 1$. As for the integrated absorbance, it is thus simply:

$$A = \int_{-\infty}^{+\infty} A_\nu \,\mathrm{d}\nu = 2\pi\alpha\eta_{ba}\omega \frac{e^{-E_a\beta}}{Z_{\mathrm{int}}} \tag{33}$$

It is independent of the line shape and can be obtained by integration of the observed spectrum to yield the value of the transition moment μ_{ba}. We have assumed that the upper state was not populated in the absence of light in order to simplify the expressions but it is easy to substract a term in which the labels a and b are exchanged. In the case of degenerate magnetic sublevels an additional sum of Clebsch–Gordan coefficients squared (1/3) in association with the square of a reduced transition moment would result from the application of Wigner–Eckart theorem [14].

3. Classical motion approach

In the classical motion limit, the thermal propagator of the off-diagonal density matrix element will be derived below but it is naturally written by introducing a classical velocity $\vec{v}$ for the external motion:

$$K_a\big(\vec{r},\vec{r}',\tau - i\hbar\beta\big) K_b^*\big(\vec{r},\vec{r}',\tau\big) \exp(-\gamma_{ba}\tau) = \exp(-E_a\beta) \exp\big[\big(i(\omega_{ba}+\delta) - \gamma_{ba}\big)\tau\big] \frac{1}{\lambda_T^3} \int \mathrm{d}^3 v\, F_M(\vec{v}) \delta\big(\vec{r}' - \vec{r} + \vec{v}\tau\big) \exp\big[-i\omega_{ba}\big(v^2/2c^2\big)\tau\big] \tag{34}$$

where the atomic frequency ω_{ba} is corrected by the recoil shift $\delta = \hbar k^2/2M$ and by the second-order Doppler effect and where $F_M(\vec{v})$ is the normalized Maxwell–Boltzmann distribution of velocities:

$$F_M(\vec{v}) = \frac{1}{(\sqrt{\pi}u)^3} \exp\left(-\frac{v^2}{u^2}\right) \tag{35}$$

More generally, we shall assume an anisotropy in the velocities corresponding for example to a molecular flow or to a difference in longitudinal and transverse temperatures

$$\frac{1}{\sqrt{\pi}u_\parallel} \frac{2v_r}{u_\perp^2} \exp\left[-\frac{v_z^2}{u_\parallel^2}\right] \exp\left[-\frac{v_r^2}{u_\perp^2}\right] \tag{36}$$

3.1. Traditional treatment with space-dependent Gaussian modes [10]

With the previous propagator the power absorbed per unit length is written as:

$$\frac{\mathrm{d}\mathfrak{P}_{abs}}{\mathrm{d}z} = \hbar\omega \frac{n^{(0)} e^{-E_a\beta}}{Z_{\mathrm{int}}} \Omega_{ba}^2 e^{-2k''(z-z_0)} \int \mathrm{d}x\,\mathrm{d}y \int \mathrm{d}^3 v\, F_M(\vec{v}) \times 2\,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, U_0^*(\vec{r}) U_0(\vec{r} - \vec{v}\tau) e^{[-i(\omega - \omega_{ba}(1 - v^2/2c^2) - \delta - kv_z) - \gamma_{ba}]\tau} \tag{37}$$

which coincides with the expression derived in [10].

In the paraxial approximation, the lowest-order Gaussian mode (TEM_{00}) corresponds to [12,15]:

$$U_0(\vec{r}) = L(z)\exp\left[-L(z)\left(x^2+y^2\right)/w_0^2\right] \tag{38}$$

The function $L(z)$ is a complex Lorentzian of z describing both the Gouy phase and the wavefront curvature of Gaussian beams:

$$L(z) = (1 - 2iz/b)^{-1} \tag{39}$$

in which b is the confocal parameter (Rayleigh length). The integration over the transverse coordinates is trivial and the resulting correlation function of τ

$$\mathcal{U}(\vec{v}\tau) = \int \mathrm{d}x\,\mathrm{d}y\,U_0^*(\vec{r})U_0(\vec{r}-\vec{v}\tau) = \frac{\pi w_0^2}{2(1+iv_z\tau/b)}\exp\left[-\frac{v_r^2\tau^2}{2w_0^2}\frac{1}{1+iv_z\tau/b}\right] \tag{40}$$

is independent of z.

The integration over the transverse velocity is also easy to perform:

$$\int_0^{+\infty}\mathrm{d}v_r\,\frac{2v_r}{u_\perp^2}\exp\left[-\frac{v_r^2}{u_\perp^2}\right]\exp\left[-i\frac{\omega_{ba}v_r^2\tau}{2c^2}\right]\mathcal{U}(\vec{v}\tau) = \frac{\pi w_0^2}{2}\frac{1}{1+iv_z\tau/b'+\frac{u_\perp^2\tau^2}{2w_0^2}+i\omega_{ba}\frac{u_\perp^2}{2c^2}\tau} \tag{41}$$

with

$$b' = b\Big/\left(1+i\omega_{ba}\frac{u_\perp^2}{2c^2}\tau\right) \tag{42}$$

and we are left with a double integral for the absorbed power per unit length:

$$\begin{aligned}\frac{\mathrm{d}\mathfrak{P}_{abs}}{\mathrm{d}z} &= \hbar\omega\frac{n^{(0)}e^{-E_a\beta}}{Z_{\mathrm{int}}}\Omega_{ba}^2e^{-2k''(z-z_0)}\frac{\pi w_0^2}{2}\\ &\quad\times 2\,\mathrm{Re}\int_0^{+\infty}\mathrm{d}\tau\int_{-\infty}^{+\infty}\mathrm{d}v_z\,\frac{1}{\sqrt{\pi}u_\parallel}e^{-\frac{v_z^2}{u_\parallel^2}}\frac{e^{[-i(\omega-\omega_{ba}-\delta-kv_z+\omega_{ba}v_z^2/2c^2)-\gamma_{ba}]\tau}}{1+iv_z\tau/b'+\frac{u_\perp^2\tau^2}{2w_0^2}+i\omega_{ba}\frac{u_\perp^2}{2c^2}\tau}\\ &= \hbar\omega\frac{n^{(0)}e^{-E_a\beta}}{Z_{\mathrm{int}}}\Omega_{ba}^2\frac{\pi w_0^2}{2}2\,\mathrm{Re}\int_0^{+\infty}\mathrm{d}\tau\,\Phi(\tau)e^{[-i(\omega-\omega_{ba}-\delta)-\gamma_{ba}]\tau}\end{aligned} \tag{43}$$

where the function $\Phi(\tau)$ is expressed in terms of the error function for complex arguments: $w(z) = e^{-z^2}\,\mathrm{erfc}(-iz)$

$$\begin{aligned}\Phi(\tau) &= \int_{-\infty}^{+\infty}\mathrm{d}v_z\,\frac{1}{\sqrt{\pi}u_\parallel}\frac{e^{-\frac{v_z^2}{u_\parallel^2}[1+i\omega_{ba}u_\parallel^2\tau/2c^2]+ikv_z\tau}}{1+iv_z\tau/b'+\frac{u_\perp^2\tau^2}{2w_0^2}+i\omega_{ba}\frac{u_\perp^2}{2c^2}\tau}\\ &= \frac{\sqrt{\pi}b'}{u_\parallel\tau}e^{\alpha\beta^2}e^{-\beta y}\,\mathrm{erfc}\left(\alpha^{1/2}\beta-\frac{1}{2}\alpha^{-1/2}y\right)\\ &= \frac{\sqrt{\pi}b'}{u_\parallel\tau}e^{-y^2/4\alpha}w\left[i\left(\alpha^{1/2}\beta-\frac{1}{2}\alpha^{-1/2}y\right)\right]\end{aligned} \tag{44}$$

with

$$\alpha = \left(1+i\omega_{ba}u_\parallel^2\tau/2c^2\right) \tag{45}$$

$$\beta = \frac{b'}{u_\parallel\tau}\left(1+\frac{u_\perp^2\tau^2}{2w_0^2}+i\omega_{ba}\frac{u_\perp^2}{2c^2}\tau\right) \tag{46}$$

$$y = ku_\parallel\tau \tag{47}$$

and neglecting the second order Doppler effect:

$$\Phi(\tau) = \frac{\sqrt{\pi}\, b}{u_\parallel \tau} e^{-(k u_\parallel \tau)^2/4} w\left[i\left(\frac{b}{u_\parallel \tau}\left(1 + \frac{u_\perp^2 \tau^2}{2w_0^2}\right) - \frac{1}{2} k u_\parallel \tau \right)\right] \tag{48}$$

If $\frac{b}{u_\parallel \tau} \gg 1$ the asymptotic expansion of the error function $\sqrt{\pi} z e^{z^2} \operatorname{erfc}(z) \sim 1$ shows that transverse transit effects play their usual role in line broadening [12,10]. However, a new remarkable result is the compensation which occurs between transverse and longitudinal transit effects when the medium is isotropic. Since $b = k w_0^2$, if $u_\perp = u_\parallel = u$, then:

$$\Phi(\tau) = \frac{\sqrt{\pi}\, b}{u\tau} e^{-(ku\tau)^2/4} w\left(i \frac{b}{u\tau}\right) \tag{49}$$

The Fourier transform of this function can be calculated from its expansion in $u\tau/b$ and we obtain the Doppler line shape with a transit correction:

$$\frac{2\sqrt{\pi}}{ku} e^{-(\omega-\omega_{ba})^2/(ku)^2}\left[1 - \frac{1}{k^2 b^2}\left(1 - 2\frac{(\omega-\omega_{ba})^2}{k^2 u^2}\right)\right] \tag{50}$$

from which we check that transit broadening is reduced to second order. The e-fold Doppler half-width is $\Delta\omega_D = ku$ and if transit effects are completely neglected as they should be, as we shall see in the next section, a Voigt profile is obtained with:

$$\Phi(\tau) = e^{-(ku\tau)^2/4} \tag{51}$$

However, if the gas is optically thick, we have seen that k was complex and should be written $k' - ik''$ in the previous function. As a result, the Voigt and also the pure Doppler profiles become distorted since an asymmetry is created by the exponential decrease of the optical field in the z-direction, which gives different accumulated Doppler phases to molecules moving upwards or downwards on the z-axis. A shift and an asymmetry are created to first order in k''/k', ratio of the optical wavelength to the optical thickness but fortunately the broadening is proportional to the square of this ratio and hence completely negligible.

3.2. Fourier-transformed laser modes and generalized Voigt profile

The previous treatment does not give a clear picture of the reason why the transit-time broadening cancels. To obtain this insight and establish this result in full generality, it is preferable to deal with the plane wave content of the laser beam:

$$U(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int \mathrm{d}^3 k\, \alpha(\vec{k}) \exp(i\vec{k}.\vec{r}) \tag{52}$$

As in Ref. [15] the functions $\alpha(\vec{k})$ may be expressed in a way which favors the z-axis as the propagation axis and obviously satisfies the propagation equation (dispersion relation):

$$\alpha(\vec{k}) = \sqrt{2\pi}\, \alpha_\perp(\vec{k}_\perp)\delta\big(k_z + \sqrt{k^2 - k_\perp^2}\,\big) \tag{53}$$

where $k = \omega/c$ is fixed by the frequency ω of the monochromatic field. To account for absorption along the z-axis, we shall simply assume as before that these functions are multiplied by $\exp[-k''(z - z_0)]$.

The expression of the absorbance becomes

$$A_\nu = 2\pi\alpha \frac{n^{(0)} d_{ba}^2 L}{Z_{\mathrm{int}}} \omega \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega+\gamma_{ba})\tau} \frac{1}{(2\pi)^3} \frac{\lambda_T^3}{SL} \int \mathrm{d}^3 r\, \mathrm{d}^3 r'\, \mathrm{d}^3 k\, \mathrm{d}^3 k'\, \alpha^*(\vec{k})\alpha\big(\vec{k}'\big) e^{-k''(z'-z)}$$
$$\times \exp i\big(\vec{k}'.\vec{r}' - \vec{k}.\vec{r}\big) K_a\big(\vec{r}, \vec{r}', \tau - i\hbar\beta\big) K_b^*\big(\vec{r}, \vec{r}', \tau\big) + \text{c.c.} \tag{54}$$

where S is the mode transverse surface

$$S = \int \mathrm{d}^2 k_\perp\, \alpha_\perp^*(\vec{k}_\perp)\alpha_\perp(\vec{k}_\perp) \tag{55}$$

If the propagators depend only on $\vec{\rho} = \vec{r}' - \vec{r}$, we can shift to the variables $\vec{r}$ and $\vec{\rho}$ and use:

$$\int \mathrm{d}^3 r \exp\bigl[i\bigl(\vec{k}' - \vec{k}\bigr).\vec{r}\bigr] = (2\pi)^2 \delta\bigl(\vec{k}'_\perp - \vec{k}_\perp\bigr) \frac{2\sin[(k_z - k'_z)L/2]}{(k_z - k'_z)} \tag{56}$$

where L is the length of the absorption path. We can perform the integrations on $\vec{r}$ and $\vec{k}'$:

$$\begin{aligned}&\frac{1}{(2\pi)^3} \int \mathrm{d}^3 r\, \mathrm{d}^3 r'\, \mathrm{d}^3 k\, \mathrm{d}^3 k'\, \alpha^*(\vec{k}) \alpha\bigl(\vec{k}'\bigr) e^{-k''(z'-z)} \exp i\bigl(\vec{k}'.\vec{r}' - \vec{k}.\vec{r}\bigr) K_a\bigl(\vec{r} - \vec{r}', \tau - i\hbar\beta\bigr) K_b^*\bigl(\vec{r} - \vec{r}', \tau\bigr) \\ &\quad = L \int \mathrm{d}^3 k\, \alpha_\perp^*(\vec{k}_\perp) \alpha_\perp(\vec{k}_\perp) \delta\bigl(k_z + \sqrt{k^2 - k_\perp^2}\bigr) \int \mathrm{d}^3 \rho \exp(i\vec{k}.\vec{\rho}) K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) e^{-k''(z'-z)}\end{aligned} \tag{57}$$

which gives for the absorbance

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{1}{S} \int \mathrm{d}^3 k\, \alpha_\perp^*(\vec{k}_\perp) \alpha_\perp(\vec{k}_\perp) \delta\bigl(k_z + \sqrt{k^2 - k_\perp^2}\bigr) \omega F_{ab}(\omega, \vec{k}) + \text{c.c.} \tag{58}$$

with

$$F_{ab}(\omega, \vec{k}) = \frac{\lambda_T^3}{Z_{\text{int}}} \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega + \gamma_{ba})\tau} \int \mathrm{d}^3 \rho\, \exp(i\vec{k}.\vec{\rho}) K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) e^{-k''(z'-z)} \tag{59}$$

Each plane wave component of the laser beam is associated only with itself in the absorption process. This is only true, of course, in linear absorption. As we shall see, when the medium is isotropic, $F_{ab}(\omega, \vec{k})$ does not depend on the direction of $\vec{k}$ but only on its modulus $|\vec{k}|$. Using the dispersion relation, we shall perform the integration $F_{ab}(\omega) = \int \mathrm{d}k_z\, \delta(k_z + \sqrt{k^2 - k_\perp^2})\, F_{ab}(\omega, \vec{k})$. Finally, the surface (55) will cancel and any dependence on the laser mode content will disappear.

Using the classical expression (34) given above for the propagator

$$\begin{aligned}F_{ab}(\omega, \vec{k}) + \text{c.c.} = \frac{\exp(-E_a\beta)}{Z_{\text{int}}} 2\,\mathrm{Re} \int \mathrm{d}^3 v\, F_M(\vec{v}) \int_0^{+\infty} \mathrm{d}\tau\, e^{k'' v_z \tau} \\ \times \exp\bigl[\bigl(-i\bigl(\omega - \omega_{ba}\bigl(1 - v^2/2c^2\bigr) - \delta - \vec{k}.\vec{v}\bigr) - \gamma_{ba}\bigr)\tau\bigr]\end{aligned} \tag{60}$$

and

$$\begin{aligned}A_\nu = 4\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_a\beta}}{Z_{\text{int}}} \frac{1}{S} \int \mathrm{d}^2 k_\perp\, \alpha_\perp^*(\vec{k}_\perp) \alpha_\perp(\vec{k}_\perp) \omega\, \mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, \frac{\exp[(-i(\omega - \omega_{ba} - \delta) - \gamma_{ba})\tau]}{(1 + i\omega_{ba}\tau u_\parallel^2/2c^2)^{1/2}(1 + i\omega_{ba}\tau u_\perp^2/2c^2)} \\ \times \exp\biggl[-\frac{k_\perp^2 u_\perp^2 \tau^2}{4(1 + i\omega_{ba}\tau u_\perp^2/2c^2)} - \frac{(k^2 - k_\perp^2) u_\parallel^2 \tau^2}{4(1 + i\omega_{ba}\tau u_\parallel^2/2c^2)}\biggr]\end{aligned} \tag{61}$$

With the isotropic velocity distribution (35) the $k_\perp$-dependence disappears:

$$\begin{aligned}&\int_0^{+\infty} \mathrm{d}\tau\, \frac{\exp[(-i(\omega - \omega_{ba} - \delta) - \gamma_{ba})\tau]}{(1 + i\omega_{ba}\tau u^2/2c^2)^{3/2}} \exp\biggl[-\frac{k^2 u^2 \tau^2}{4(1 + i\omega_{ba}\tau u^2/2c^2)}\biggr] \\ &\quad = \int \mathrm{d}^3 v\, \frac{F_M(\vec{v})}{(i(\omega - \omega_{ba}(1 - v^2/2c^2) - \delta - \vec{k}.\vec{v}) + \gamma_{ba})} = \frac{\sqrt{\pi}}{ku} z(\zeta, u/2c)\end{aligned} \tag{62}$$

where we have introduced a generalization of the Voigt profile to include the second-order Doppler effect. The reduced variable is

$$\zeta = \xi + i\eta = \bigl[(\omega - \omega_{ba} - \delta) + i\gamma_{ba}\bigr]/\Delta\omega_D \tag{63}$$

The new function $z(\zeta, u/2c)$ is the convolution of the Gaussian distribution $F_M(\vec{p})$ and of the shifted Lorentzian. The absorbance is

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_a\beta}}{Z_{\rm int}} \frac{2\omega\sqrt{\pi}}{ku} \operatorname{Re} z(\zeta, u/2c) \tag{64}$$

There is no transit broadening in this line shape, which reduces to the usual Voigt profile when the second-order Doppler effect is neglected:

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_a\beta}}{Z_{\rm int}} \frac{2\omega\sqrt{\pi}}{ku} \operatorname{Re} w(\zeta) \tag{65}$$

The influence of the second-order Doppler effect is easily seen with Mathematica and shows up as an asymmetry without significant broadening. The same conclusion results from a complex k in the case of an optically thick gas as discussed above. These conclusions hold without any assumption on the mode structure of the optical beam. To recover and extend the result derived in the previous section, the functions $\alpha(\vec{k})$ may be expanded on the complete basis of Hermite–Gauss functions without any loss of generality [12,15]. For the lowest-order Gaussian mode (higher-order modes can be dealt with by keeping Hermite polynomials):

$$\alpha(\vec{k}) = \sqrt{2\pi}\,\alpha_\perp(\vec{k}_\perp)\delta\big(k_z + \sqrt{k^2 - k_\perp^2}\big) = \frac{\sqrt{2\pi}}{\Delta^2} \exp\left(-\frac{k_\perp^2}{2\Delta^2}\right)\delta\big(k_z + \sqrt{k^2 - k_\perp^2}\big) \tag{66}$$

The paraxial approximation uses the expansion:

$$\sqrt{k^2 - k_\perp^2} \to k - k_\perp^2/2k \tag{67}$$

and the usual structure of the Gaussian modes is easily derived by calculating the Fourier transform as in Refs. [12,15]. This calculation gives the relation between the parameter Δ and the beam waist radius: $\Delta = \sqrt{2}/w_0$. The isotropy of space is obviously broken either by this paraxial approximation or by a non-isotropic velocity distribution and the absorbance is given by:

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_a\beta}}{Z_{\rm int}} 2\omega \operatorname{Re} \int_0^{+\infty} \mathrm{d}\tau\, \Phi(\tau) e^{-i\omega\tau} \exp\big[\big(i(\omega_{ba} + \delta) - \gamma_{ba}\big)\tau\big] \tag{68}$$

where one recovers the function $\Phi(\tau)$ calculated above, which is now an integral over $k_\perp^2$:

$$\Phi(\tau) = \frac{1}{\pi\Delta^2} \frac{1}{(1 + i\omega_{ba}\tau u_\parallel^2/2c^2)^{1/2}(1 + i\omega_{ba}\tau u_\perp^2/2c^2)} \int \mathrm{d}^2 k_\perp \exp\left(-\frac{k_\perp^2}{\Delta^2}\right) \times \exp\left[-\frac{k_\perp^2 u_\perp^2 \tau^2}{4(1 + i\omega_{ba}\tau u_\perp^2/2c^2)} - \frac{(k - k_\perp^2/2k)^2 u_\parallel^2 \tau^2}{4(1 + i\omega_{ba}\tau u_\parallel^2/2c^2)}\right] \tag{69}$$

easily calculated with the same result (44). This shows that a transit broadening is artificially introduced when we break the isotropy of space by the paraxial approximation.

4. Quantized molecular motion approach

In a fully quantized treatment of the molecular motion the propagators can be written as simple exponentials and Gaussians in the case of Hamiltonians at most quadratic in position and momentum operators, thanks to *ABCD* matrices [15,16,5,17]:

$$K\big(\vec{r}, \vec{r}', t - t'\big) = \left(\frac{M}{2\pi i\hbar}\right)^{3/2} |\det B|^{-1/2} \exp[i S_c/\hbar] \tag{70}$$

where S_c is the classical action integral. In the case of free flight, these propagators are easy to calculate from the kinetic energy operator and are functions of $\vec{\rho} = \vec{r}' - \vec{r}$ only:

$$K_\alpha\big(\vec{r}, \vec{r}', \tau\big) = \exp(-i E_\alpha \tau/\hbar)\left(\frac{M_\alpha}{2\pi i\hbar\tau}\right)^{3/2} \exp\left[\left(\frac{i M_\alpha}{2\hbar\tau}\right)\big(\vec{r} - \vec{r}'\big)^2\right] \tag{71}$$

with $M_\alpha = E_\alpha/c^2$. The thermal propagator for the off-diagonal density matrix element is then:

$$\lambda_T^3 K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) = \lambda_T^3 \exp(-E_a\beta) \exp[i\omega_{ba}\tau] \left(\frac{M_a}{2\pi i\hbar(\tau - i\hbar\beta)}\right)^{3/2} \left(-\frac{M_b}{2\pi i\hbar\tau}\right)^{3/2} \times \exp\left[\frac{i}{2\hbar}\left(\frac{M_a}{(\tau - i\hbar\beta)} - \frac{M_b}{\tau}\right)\rho^2\right] \tag{72}$$

The spatial Fourier transform is

$$\lambda_T^3 \int \mathrm{d}^3\rho \, \exp(i\vec{k}.\vec{\rho}) K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) = \exp(-E_a\beta) \frac{\exp[i\omega_{ba}\tau]}{(1 + i\omega_{ba}\tau u^2/2c^2)^{3/2}} \exp\left[-\frac{|\vec{k}|^2 u^2 \tau(\tau - i\hbar\beta)}{4(1 + i\omega_{ba}\tau u^2/2c^2)}\right] \tag{73}$$

Here again, thanks to isotropy, $F_{ab}(\omega, \vec{k})$ is independent of the direction of $\vec{k}$ and taking into account the dispersion relation this leads to a function $F_{ab}(\omega)$ of ω only.

This gives for the absorbance

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{1}{S} \int \mathrm{d}^3k \, \alpha_\perp^*(\vec{k}_\perp)\alpha_\perp(\vec{k}_\perp)\delta\big(k_z + \sqrt{k^2 - k_\perp^2}\big)\omega F_{ab}(\omega, \vec{k}) + \text{c.c.} = 4\pi\alpha n^{(0)} d_{ba}^2 L\omega \,\mathrm{Re}\, F_{ab}(\omega) \tag{74}$$

We recover the generalized Voigt profile by adding a decay constant γ_{ba} in the propagators. The recoil shift $\delta = \hbar\beta k^2 u^2/4 = \hbar k^2/2M$ comes out naturally as well as the second-order Doppler shift and broadening:

$$F_{ab}(\omega) + \text{c.c.} = \frac{\exp(-E_a\beta)}{Z_{\text{int}}} 2\,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau \, \frac{\exp[-i(\omega - \omega_{ba})\tau - \gamma_{ba}\tau]}{(1 + i\omega_{ba}\tau u^2/2c^2)^{3/2}} \exp\left[-\frac{k^2 u^2 \tau(\tau - i\hbar\beta)}{4(1 + i\omega_{ba}\tau u^2/2c^2)}\right] \tag{75}$$

If we use other choices for the propagator, e.g. the expression corresponding to harmonic traps [15,17], we find the usual MLD narrowing in a trap. With this theoretical approach the diagram of Fig. 1 is really treated as an interferometer, in which atom waves propagate and interfere.

4.1. Classical limit of the propagator and connection with Van Hove's self-diffusion function

In the limit $h \to 0$ the thermal density matrix propagator

$$\lambda_T^3 K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) \exp(-\gamma_{ba}\tau) = \lambda_T^3 \exp(-E_a\beta) \exp\big[-i(\omega_{ba} - i\gamma_{ba})\tau\big] \left(\frac{M_a}{2\pi i\hbar(\tau - i\hbar\beta)}\right)^{3/2} \left(-\frac{M_b}{2\pi i\hbar\tau}\right)^{3/2} \times \exp\left[\frac{i}{2\hbar}\left(\frac{M_a}{(\tau - i\hbar\beta)} - \frac{M_b}{\tau}\right)\rho^2\right] \tag{76}$$

goes to

$$\exp(-E_a\beta) \exp\big[\big(i(\omega_{ba} + \delta) - \gamma_{ba}\big)\tau\big] \int \mathrm{d}^3v \, F_M(\vec{v})\delta(\vec{\rho} + \vec{v}\tau) \exp\big[-i\omega_{ba}\big(v^2/2c^2\big)\tau\big] \tag{77}$$

As expected for a quantum correction, the recoil shift does not come out naturally in this approximation. We have maintained it artificially on the basis of the equation satisfied by the density matrix elements derived in [10]. Another way to obtain a classical propagator and still to retrieve this shift is described now.

First let us make the link with the Van Hove self-correlation function G_s [21]. We introduce the propagator $K(\vec{\rho}, \tau)$ for a particle with a single mass M such that

$$K_a(\vec{\rho}, \tau - i\hbar\beta) K_b^*(\vec{\rho}, \tau) \exp(-\gamma_{ba}\tau) = \exp(-E_a\beta) \exp\big[\big(i(\omega_{ba} + \delta) - \gamma_{ba}\big)\tau\big] \exp\big[-i\omega_{ba}\rho^2/\big(2\hbar c^2\tau\big)\big] \times K(\vec{\rho}, \tau - i\hbar\beta) K^*(\vec{\rho}, \tau) \tag{78}$$

or

$$K_\alpha(\vec{\rho},\tau) = \exp[-iE_\alpha\tau/\hbar]\exp\left[i(\Delta E_\alpha)\rho^2/\left(2\hbar c^2\tau\right)\right]K(\vec{\rho},\tau) \tag{79}$$

We have factorized all complex phase factors including the relativistic correction corresponding to the mass change $\Delta E_\alpha/c^2$. Then, using our exact quantum propagator, one finds that Van Hove self-correlation function G_s is given by:

$$G_s(\vec{\rho},\tau) = \lambda_T^3 K(\vec{\rho},\tau - i\hbar\beta)K^*(\vec{\rho},\tau) = \frac{1}{(2\pi)^{3/2}R^3(\tau)}\exp\left[-\frac{\rho^2}{2R^2(\tau)}\right] \tag{80}$$

with

$$\sqrt{2}\,R(\tau) = u\left(\tau^2 - i\hbar\beta\tau\right)^{1/2} \tag{81}$$

Because of its complex character the function $G_s(\vec{\rho},\tau)$ does not have a clear classical interpretation but as suggested in [21] we may introduce instead the real function[2]:

$$F_s(\vec{\rho},\tau) = G_s(\vec{\rho},\tau + i\hbar\beta/2) \tag{85}$$

which plays the role of a classical probability of finding the particle after the time τ at the position $\vec{\rho}$. Eq. (59) gives:

$$\begin{aligned}
F_{ab}(\omega,\vec{k}) + \text{c.c.} &= \frac{\lambda_T^3}{Z_{\text{int}}}\int_{-\infty}^{+\infty} d\tau\, e^{-i\omega\tau}\int d^3\rho\, \exp(i\vec{k}.\vec{\rho})\exp(-E_a\beta) \\
&\quad\times\exp\left[\left(i\omega_{ba}\tau - \gamma_{ba}|\tau|\right)\right]\exp\left[-i\omega_{ba}\rho^2/\left(2c^2\tau\right)\right]K(\vec{\rho},\tau - i\hbar\beta)K^*(\vec{\rho},\tau) \\
&= \frac{\exp(-E_a\beta)}{Z_{\text{int}}}e^{\hbar\beta(\omega-\omega_{ba})/2}\int_{-\infty}^{+\infty} d\tau\, e^{-i(\omega-\omega_{ba})\tau-\gamma_{ba}|\tau|}\int d^3\rho\, \exp(i\vec{k}.\vec{\rho}) \\
&\quad\times\exp\left[-i\omega_{ba}\rho^2/\left(2c^2\tau\right)\right]\lambda_T^3 K(\vec{\rho},\tau - i\hbar\beta/2)K^*(\vec{\rho},\tau + i\hbar\beta/2) \\
&= \frac{\exp(-E_a\beta)}{Z_{\text{int}}}e^{\hbar\beta(\omega-\omega_{ba})/2}\int_{-\infty}^{+\infty} d\tau\, e^{-i(\omega-\omega_{ba})\tau-\gamma_{ba}|\tau|}\int d^3\rho\exp(i\vec{k}.\vec{\rho}) \\
&\quad\times\exp\left[-i\omega_{ba}\rho^2/\left(2c^2\tau\right)\right]F_s(\vec{\rho},\tau)
\end{aligned} \tag{86}$$

with

$$F_s(\vec{\rho},\tau) = \frac{1}{(2\pi)^{3/2}R^3(\tau)}\exp\left[-\frac{\rho^2}{(2R^2(\tau))}\right] \tag{87}$$

It would be natural to take

$$F_s(\vec{\rho},\tau) = \int d^3v\, F_M(\vec{v})\delta(\vec{\rho} + \vec{v}\tau) \tag{88}$$

[2] To see that the natural complex variable is indeed $\theta = \tau + i\hbar\beta/2$, we should compare the Liouville–von Neumann and Bloch equations for the density matrix:

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho] \tag{82}$$

$$\frac{\partial\rho}{\partial\beta} = -\frac{1}{2}\left\{H - \langle E\rangle,\rho\right\} \tag{83}$$

Both equations can be combined as a single equation with respect to the complex time θ:

$$i\hbar\frac{\partial\rho}{\partial\theta} = \left(H - \langle E\rangle\right)\rho \tag{84}$$

and its Hermitian conjugate partner.

However this probability has no width for $\tau = 0$ and a finite quantum extension should be added to the classical width corresponding to Heisenberg's uncertainty for a particle with velocity u. From (81) and the shift $\tau \to \tau + i\hbar\beta/2$ we get:

$$R^2(\tau) = u^2\tau^2 + \lambda_T^2/8\pi \tag{89}$$

When this is done the final result has the same recoil shift as what is obtained by using the factor $\exp[i\delta\tau]$ in the classical propagator.

4.2. Galatry's profile [28]

Up to this point we have treated relaxation in a very crude manner with a simple relaxation constant of the optical dipole. Collisions also affect the external motion of molecules. We shall first introduce this possibility in a classical approach describing the effect of collisions on the classical motion of molecules and turn later to a quantum-mechanical treatment by collision kernels. For this we reproduce the same approach as in the previous paragraph where, this time, the classical self-diffusion function

$$F_s(\vec{\rho}, \tau) = \frac{1}{(2\pi)^{3/2}R^3(\tau)} \exp\left[-\frac{\rho^2}{(2R^2(\tau))}\right] \tag{90}$$

is taken from the work of S. Chandrasekhar [22,26] on Brownian motion and is obtained by the Langevin equation

$$R^2(\tau) = \frac{2D}{\beta'}\left[\beta'\tau - 1 + \exp\left(-\beta'\tau\right)\right] + \lambda_T^2/8\pi \tag{91}$$

$$\beta' = \frac{1}{\beta DM} = \frac{u^2}{2D} \tag{92}$$

where D is the self-diffusion constant of the gas. The spatial Fourier transform is:

$$\begin{aligned}
&\int \mathrm{d}^3\rho\, \exp(i\vec{k}.\vec{\rho}) \exp\left[-i\omega_{ba}\rho^2/\left(2c^2\tau\right)\right] F_s(\vec{\rho}, \tau) \\
&\quad = \frac{1}{(2\pi)^{3/2}R^3(\tau)} \int \mathrm{d}^3\rho\, \exp(i\vec{k}.\vec{\rho}) \exp\left[-\left(\frac{1}{R^2(\tau)} + \frac{i\omega_{ba}}{c^2\tau}\right)\frac{\rho^2}{2}\right] \\
&\quad = \frac{1}{(1 + i\omega_{ba}R^2/c^2\tau)^{3/2}} \exp\left[-\frac{|\vec{k}|^2R^2(\tau)}{2(1 + i\omega_{ba}R^2/c^2\tau)}\right]
\end{aligned} \tag{93}$$

Finally

$$F_{ab}(\omega) = \frac{\exp(-E_a\beta)}{Z_{\mathrm{int}}} e^{\hbar\beta(\omega-\omega_{ba})/2} \int_0^{+\infty} \mathrm{d}\tau\, \frac{e^{-i(\omega-\omega_{ba})\tau-\gamma_{ba}|\tau|}}{(1 + i\omega_{ba}R^2/c^2\tau)^{3/2}} \exp\left[-\frac{k^2R^2(\tau)}{2(1 + i\omega_{ba}R^2/c^2\tau)}\right] \tag{94}$$

and

$$A_\nu = 4\pi\alpha n^{(0)} d_{ba}^2 L\omega\, \mathrm{Re}\, F_{ab}(\omega) \tag{95}$$

If we ignore the second-order Doppler effect and reduce the recoil effect to a simple shift, we get Galatry's profile:

$$\begin{aligned}
F_{ab}(\omega) + \mathrm{c.c.} &= \frac{\exp(-E_a\beta)}{Z_{\mathrm{int}}} 2\,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, e^{-i(\omega-\omega_{ba})\tau-\gamma_{ba}\tau} \exp\left\{-\frac{k^2u^2}{2\beta'^2}\left[\beta'\tau - 1 + \exp\left(-\beta'\tau\right)\right]\right\} \\
&= \frac{\exp(-E_a\beta)}{Z_{\mathrm{int}}} \frac{2}{ku}\, \mathrm{Re}\, \frac{1}{y(\xi)}\, {}_1F_1\left[1, 1 + y/a; \frac{1}{2a^2}\right]
\end{aligned} \tag{96}$$

where ${}_1F_1$ is Kummer confluent hypergeometric function and

$$a = \frac{\beta'}{\Delta\omega_D}; \qquad y(\xi) = \frac{1}{2a} + \eta - i\xi \tag{97}$$

This profile evolves from the Voigt profile in the low pressure range to a Lorentzian shape in the high pressure limit with a substantial reduction of the Doppler width. It is expected to be a faithful description of the lineshape only in the limit of soft collisions with a light perturber.

5. Introduction of collision kernels in the density matrix equations

To introduce relaxation by external perturbers in a quantum mechanical way it is necessary to take a trace over the external reservoir and hence to give up the description of our two-level system by wave functions and to use instead a reduced density matrix formalism.

Density matrix equations which include momentum-changing collisions can be derived rigorously from the knowledge of individual collision events [18,19]. It is easier to deal with these collisions in the momentum representation. Thus, using Eq. (4), let us first rewrite the expression for the absorbance in this representation:

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_a\beta}}{Z_{\rm int}} 2\omega \,\mathrm{Re} \int_0^{+\infty} \mathrm{d}\tau\, e^{-(i\omega+\gamma_{ba})\tau} \int \mathrm{d}^3k\, \mathrm{d}^3k'\, \alpha^*(\vec{k})\alpha\big(\vec{k}'\big) \times \int \mathrm{d}^3p_0\, \mathrm{d}^3p\, K_a(\vec{p}_0 \to \vec{p},\tau) K_b^*\big(\vec{p}_0 + \hbar\vec{k}' \to \vec{p} + \hbar\vec{k},\tau\big) F_M(\vec{p}_0) \tag{98}$$

where $F_M(\vec{p}_0)$ is the Maxwell–Boltzmann distribution of momenta corresponding to $F_M(\vec{v})$. As stated above, the propagator $K_a K_b^*$ of the off-diagonal density matrix element needs to be averaged over collisions with perturbers P and we replace it by a Green function $\mathcal{G}'_{ab}(\vec{p}_0 \to \vec{p}, \vec{p}_0 + \hbar\vec{k}' \to \vec{p} + \hbar\vec{k}, \tau)$ such that:

$$\mathcal{G}'_{ab}\big(\vec{p}_0 \to \vec{p}, \vec{p}_0 + \hbar\vec{k}' \to \vec{p} + \hbar\vec{k}, \tau\big) = \big\langle K_a(\vec{p}_0 \to \vec{p},\tau) K_b^*\big(\vec{p}_0 + \hbar\vec{k}' \to \vec{p} + \hbar\vec{k}, \tau\big)\big\rangle_P \theta(\tau) \tag{99}$$

(the Heaviside step function $\theta(\tau)$ transforms a propagator into a Green function)

$$\mathcal{G}'_{ab}\big(\vec{p}_0 \to \vec{p}, \vec{p}_0 + \hbar\vec{k}' \to \vec{p} + \hbar\vec{k}, \tau\big) = \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \tau)\delta\big(\vec{k}' - \vec{k}\big) \tag{100}$$

The distribution $\delta(\vec{k}' - \vec{k})$ has been introduced to reflect the fact that collisions do not create any additional spatial modulation since they act uniformly and isotropically. The new Green function $\mathcal{G}_{ab}$ satisfies the integro-differential equation (the relaxation factor $\exp(-\gamma_{ab}\tau)$ is now included in this function):

$$\frac{\partial \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \tau)}{\partial\tau} + \big(i\omega_{ab}\big(1 - p^2/2M^2c^2\big) - i\vec{k}.\vec{p}/M - i\delta + \gamma_{ab}\big)\mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \tau) = \delta(\vec{p} - \vec{p}_0)\delta(\tau) + \int \mathrm{d}^3p'\, W_{ab}\big(\vec{p}' \to \vec{p}\big)\mathcal{G}_{ab}\big(\vec{p}_0 \to \vec{p}', \vec{k}, \tau\big) \tag{101}$$

where $W_{ab}(\vec{p}' \to \vec{p})$ is the collision kernel describing the probability for a momentum change from $\vec{p}'$ to $\vec{p}$. Finally

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 \frac{L}{S} \frac{e^{-E_a\beta}}{Z_{\rm int}} \omega \int_{-\infty}^{+\infty} \mathrm{d}\tau\, e^{-i\omega\tau} \int \mathrm{d}^3k\, \alpha^*(\vec{k})\alpha(\vec{k}) \int \mathrm{d}^3p_0\, \mathrm{d}^3p\, \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \tau) F_M(\vec{p}_0) + \text{c.c.}$$

$$= 2\pi\alpha n^{(0)} d_{ba}^2 \frac{L}{S} 2\omega \int \mathrm{d}^3k\, \alpha^*(\vec{k})\alpha(\vec{k})\, \mathrm{Re}\, F_{ab}(\omega, \vec{k}) \tag{102}$$

with

$$F_{ab}(\omega, \vec{k}) = \frac{e^{-E_a\beta}}{Z_{\rm int}} \int \mathrm{d}^3p_0\, \mathrm{d}^3p\, \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \omega) F(\vec{p}_0) = \frac{e^{-E_a\beta}}{Z_{\rm int}} \int \mathrm{d}^3p\, f_{ab}(\vec{p}, \vec{k}, \omega) \tag{103}$$

where we have introduced the Fourier transforms:

$$\mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \omega) = \int_{-\infty}^{+\infty} \mathrm{d}\tau\, e^{-i\omega\tau} \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \tau) \tag{104}$$

$$f_{ab}(\vec{p}, \vec{k}, \omega) = \int \mathrm{d}^3p_0\, \mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \omega) F_M(\vec{p}_0) \tag{105}$$

which satisfy respectively

$$\begin{aligned}&\big(i\omega - i\omega_{ba}\big(1 - p^2/2M^2c^2\big) - i\vec{k}.\vec{p}/M - i\delta + \gamma_{ab}\big)\mathcal{G}_{ab}(\vec{p}_0 \to \vec{p}, \vec{k}, \omega)\\&\quad = \delta(\vec{p} - \vec{p}_0) + \int \mathrm{d}^3p'\, W_{ab}\big(\vec{p}' \to \vec{p}\big)\mathcal{G}_{ab}\big(\vec{p}_0 \to \vec{p}', \vec{k}, \omega\big)\end{aligned} \tag{106}$$

and

$$\begin{aligned}&\big(i\omega - i\omega_{ba}\big(1 - p^2/2M^2c^2\big) - i\vec{k}.\vec{p}/M - i\delta + \gamma_{ab}\big) f_{ab}(\vec{p}, \vec{k}, \omega)\\&\quad = F_M(\vec{p}) + \int \mathrm{d}^3p' W_{ab}\big(\vec{p}' \to \vec{p}\big) f_{ab}\big(\vec{p}', \vec{k}, \omega\big)\end{aligned} \tag{107}$$

Generally this last equation will be solved numerically from a numerical calculation of the collision kernels [29, 30,23,25]. There is, however, a simple case where it can be solved analytically. This is the model of Nelkin and Ghatak [20] in which each collision is assumed to be strong enough to redistribute the momenta according to the Maxwell–Boltzmann distribution:

$$W_{ab}\big(\vec{p}' \to \vec{p}\big) = \alpha F_M(\vec{p}) \tag{108}$$

where α is an adjustable collision frequency. Hence:

$$f_{ab}(\vec{p}, \vec{k}, \omega) = \frac{F_M(\vec{p})(1 + \alpha \int \mathrm{d}^3p'\, f_{ab}(\vec{p}', \vec{k}, \omega))}{(i\omega - i\omega_{ba}(1 - p^2/2M^2c^2) - i\vec{k}.\vec{p}/M - i\delta + \gamma_{ab})} \tag{109}$$

and by integration over $\vec{p}$:

$$\begin{aligned}&\int \mathrm{d}^3p\, f_{ab}(\vec{p}, \vec{k}, \omega)\\&\quad = \left(1 + \alpha \int \mathrm{d}^3p\, f_{ab}(\vec{p}, \vec{k}, \omega)\right) \int \mathrm{d}^3p\, \frac{F_M(\vec{p})}{(i\omega - i\omega_{ba}(1 - p^2/2M^2c^2) - i\vec{k}.\vec{p}/M - i\delta + \gamma_{ab})}\\&\quad = \frac{\sqrt{\pi}}{ku}\left(1 + \alpha \int \mathrm{d}^3p\, f_{ab}(\vec{p}, \vec{k}, \omega)\right) z(\zeta, u/2c)\end{aligned} \tag{110}$$

we obtain the generalized Nelkin–Ghatak profile:

$$2\,\mathrm{Re}\, F_{ab}(\omega, \vec{k}) = \frac{e^{-E_a\beta}}{Z_{\mathrm{int}}} 2\,\mathrm{Re} \int \mathrm{d}^3p\, f_{ab}(\vec{p}, \vec{k}, \omega) = \frac{2\sqrt{\pi}}{ku} \frac{e^{-E_a\beta}}{Z_{\mathrm{int}}}\,\mathrm{Re}\, \frac{z(\zeta, u/2c)}{1 - \alpha(\sqrt{\pi}/ku) z(\zeta, u/2c)} \tag{111}$$

As we have seen before, in the case of an isotropic medium, $F_{ab}(\omega, \vec{k})$ does not depend on the direction of $\vec{k}$ but only on its modulus, so that the dispersion relation between this modulus and $k = \omega/c$ gives a function $F_{ab}(\omega)$ of ω only. As before $S = \int \mathrm{d}^2k_\perp\, \alpha_\perp^*(\vec{k}_\perp)\alpha_\perp(\vec{k}_\perp)$ is the transverse beam surface and the absorbance

$$A_\nu = 4\pi\alpha n^{(0)} d_{ba}^2 L\omega\,\mathrm{Re}\, F_{ab}(\omega) \tag{112}$$

is independent of the mode content of the light beam and hence has no additional transit time broadening.

Using this quantized approach, one can also retrieve Galatry's profile. For this purpose, the Boltzmann equation is approximated by a Fokker–Planck equation obtained by an expansion of the collision kernel [27]. This Fokker–Planck equation is then solved [31] and yields Galatry's profile derived above classically.

As it is well known both Nelkin–Ghatak and Galatry's profiles are very similar and both lead to MLD narrowing. They differ by the significance and knowledge of the parameters β' and α. More work has to be done to compare these models to purely numerical calculations treating the collisions more rigorously and above all to experiments in the critical regime where the collisional width and the Doppler width are comparable.

6. Conclusion

We have demonstrated an important property concerning the absorption profile of a low-pressure gas: the absence of any additional transit broadening independently of the optical quality of the laser beam wavefronts and effective diameters if the medium is homogeneous and isotropic without nearby walls or potentials susceptible to interfere with the absorption process. We have generalized the usual Voigt, Galatry and Nelkin–Ghatak profiles to include both the recoil shift and the second-order Doppler shift. If this turns out to be necessary, we know how to calculate rigorously the collision kernels from the intermolecular potentials and from there the absorption profile in the low-pressure regime. This has been done with some success in saturation spectroscopy [24,29,30,23,25]. However, thanks to the line shape independence from the geometry of the laser beams, the very low pressure limit appears favorable to the determination of the Boltzmann constant and one should not need to calculate very accurately the corrections coming from collision physics including the MLD narrowing.

Acknowledgements

The author gratefully acknowledges critical reading of this manuscript and useful suggestions by Anne Amy-Klein, Jean Dalibard, Christophe Daussy, Benoît Darquié and Cyril Lemarchand.

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