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Pressure Line Shape and the Dicke Effect

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Our main purpose in this paper is to calculate the shape of spectral lines for gases taking into account simultaneously the reduction of the Doppler effect and the perturbation of the interna1 energy levels produced by molecular interactions. Considering both effects, we obtain a general expression for the line shape. This general result is applied in some particular cases.

A principal finalidade dêste trabalho é calcular a forma de linhas espectrais em gases levando em conta simultâneamente a redução da largura Doppler e a perturbação dos níveis internos de energia provocadas por interações moleculares Considerando ambos os efeitos, obtivemos uma expressão geral para a forma da linhaeEste resultado geral é aplicado a alguns casos particulares.

1. Introduction

As is well knownls2,the main purpose of the line shape studies is to obtain information on the many-body behaviour and on the structure of a complex system. This information is obtained by relating the line shape, obtained from spectroscopical measurements, to the statistical-mechanical calculations.

Some theoretical works[3,4] on the line shape have been performed by considering general cluster expansions of the relaxation function. They give a good insight into the nature of the phenomenon, but for practical calculations it is necessary to use models based on physical considerations, which allow one to extract from such expansions only that part which is relevant to the special physical situation and for which quantitative results may be evaluated. These special physical situations will be considered only in Section 3 and the general case in Section 2.

Molecular[5] interactions have two effects on line shapes: (1) the Doppler width and recoil shift are reduced and (2) the lines are shifted and broa-

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dened due to the perturbation of the internal energy levels. The reduction of the Doppler width and recoil shift in gases will be named Dicke Effect[6] or Mossbauer Effect[7] in gases.

Many authors[8-11], using purely quantum mechanical methods, treated accurately the line shape problem for gases at low pressures and high temperatures. However, they considered only the perturbation of the internal energy levels. In a recent paper[2], the Doppler contribution was obtained, but the reduction of the Doppler width was not considered. In our preceding paper[12], we have briefly shown how to take into account, for gases at low pressures and high temperatures, both the Dicke effect and the perturbation of the internal energy levels. The reduction of the Doppler width in gases[6*'] was calculated neglecting the perturbation of the internal energy levels.

Using the usual statistical-mechanical formalism and taking into account both the Dicke effect and the perturbation of the internal energy Ievels, a general expression for the line shape in gases is calculated in Section 2 In Section 3, we apply the results of Section 2 in some special circumstances. In this Section, we also discuss the main hypothesis assumed in the preceding paper[12].

2. Line Shape in a General Case

Let us consider a system which is a mixture of two kinds of molecules, which we distinguish by the indices 1 and 2. We assume that only particles 1 interact with the incident radiation field. This means that, in our theory, the molecules 2 have no resonance at the frequency of the incident radiation wave. The molecules 1 are called emitting or radiating and the 2 are called perturbing.

If there is only one molecule of the type 1, the total Hamiltonian of the system may be written

$$H = H_0 + V + H_R + H_{1R}, \tag{1}$$

where

$$H_0 = T^{(1)} + G^{(1)} + \sum_{j=1}^{N^{(2)}} (T_j^{(2)} + G_j^{(2)}) = H_1 + H_2, \tag{2}$$

is the Hamiltonian of the free particles, T and G are the kinetic and internal energy operators, respectively, V the interaction between all molecules of

the system, H_R the Hamiltonian of the free radiation field and $H_{,,} = -d_1 \cdot \mathbf{E}$ the interaction between the radiation field E (electric or magnetic) with the dipole moment $\mathbf{d}_1$ (electric or magnetic) of the emitting particle.

When the intensity of the incident radiation field is too high, transitions among the molecular states are then induced at a rate that is not negligible compared with the collision rate, thus invalidating the assumption of thermal equilibrium. It can be shown[13,14,15] that the broadening of an absorption line is not attributed to any intrinsic modifications of the line shape, but rather to a frequency dependent alteration of the energy level populations. This is known as "saturation effect". As we consider only weak radiation fields, this effect will be neglected.

The eigenfunctions and eigenvalues of the operator H, will be indicated by $|\eta(N_{k'}, \ldots, N_k, \ldots))$ and $\sum_k \tilde{A}ck\, N_k$, respectively, where N_k is the number of photons with energy $\hbar kc = \hbar\omega$.

Among all interna1 states of the emitting molecule, we separate those, here indicated by $|\psi_n\rangle$, which participate in the transitions whose shapes we wish to analyse. Defining the operator $h^{(1)}$, such that $h^{(1)}|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$, we write $G^{(1)} = h^{(1)} + G'^{(1)}$. If we are interested, for instance, in the rotational transitions, $h^{(1)}$ would be the rotational energy operator and $|\psi_n\rangle$ the rotational energy states.

We assume that the state 'of the molecular system can be described by $|\psi_n\rangle|\phi_m\rangle$, where $|\phi_m\rangle$ takes into account all degrees of freedom of the molecular system excluding those of the operator $h^{(1)}$. Of course, this is a zeroth-order approximation wave function for the system; higher order approximations can be obtained considering the interaction' potential between the emitting particles and using perturbation theory, which will be done in what follows.

The time evolution operator of the total system, molecules and radiation field, will be indicated by $U(t, t')$. It obeys the equation $i\hbar \frac{\partial}{\partial t} U(t, t') = = \mathrm{H}U(t, t')$.

Putting, for simplicity, $t' = 0$ the transition probability dP_{if}^{IF} between the states

$$|\Psi_{iI}(0)\rangle = |\psi_i\rangle|\phi_I\rangle|\eta(\ldots N_k \ldots)\rangle$$

and $|\Psi_{fF}(t_0)\rangle = |\psi_f(t_0)\rangle\,|\phi_F(t_0)\rangle\,|\eta(\ldots N_k + 1\ldots, t_0)\rangle$, in the time interval $t - t' = t_0$, is given by

$$dP_{if}^{IF} = |\langle\phi_F(t_0)|\langle\psi_f(t_0)|\langle\eta(\ldots N_k + 1\ldots t_0)|\,U(t_0)|\cdot \cdot|\eta(\ldots N_k\ldots)\rangle|\,\psi_i\rangle\,|\,\phi_I\rangle|^2 \qquad (3)$$

where $U(t_0) = U(t, t' = 0)$.

Indicating by $U_{mR}(t, t')$ the time evolution operator that obeys the equation $i\hbar\partial U_{mR}(t, t')/\partial t = H_{mR}\,U_{mR}(t, t')$, where $H_{mR} = H_0 + V + H_R$, we have:

$$dP_{if}^{IF} = |\langle\phi_F|\langle\psi_f|\langle\eta(\ldots N_k + 1\ldots)|\,U_{mR}^{\dagger}(t_0)\,U(t_0)|\cdot \cdot|\eta(\ldots N_k\ldots)\rangle|\,\psi_i\rangle\,|\,\phi_I\rangle|^2 . \qquad (4)$$

Let us write $U_{mR}^{\dagger}(t_0)\,U(t_0)$ in a different form Putting $W = U_{mR}^{\dagger}\,U$, we obtain

$$\dot{W} = \dot{U}_{mR}^{\dagger}\,U + U_{mR}^{\dagger}\,\dot{U} = \frac{1}{i\hbar}\,U_{mR}^{\dagger}(-H_{mR}\,U + HU) = \frac{i}{\hbar}\,U_{mR}^{\dagger}\,H_{1R}\,U_{mR}\,W. \qquad (5)$$

Solving equation (5) by sucessive approximations, we obtain, considering only the first order term in $|\mathbf{E}|$:

$$W(t_0) = 1 + \frac{1}{i\hbar}\int_0^{t_0} U_{mR}^{\dagger}(t)\,H_{1R}\,U_{mR}(t)\,dt. \qquad (6)$$

So, substituting (6) into (5), as the term 1 gives no contribution, we get:

$$dP_{if}^{IF} = \frac{1}{\hbar^2}\left|\int_0^{t_0}\langle\phi_F|\langle\psi_f|\langle\eta(\ldots N_k + 1\ldots)|\,U_{mR}^{\dagger}(t)\,H_{1R}\,U_{mR}(t)\cdot \cdot|\eta(\ldots N_k\ldots)\rangle|\,\psi_i\rangle\,|\,\phi_I\rangle|^2 . \qquad (7)$$

Now, the vector potential $\mathbf{A}(\mathbf{r}, t)$ is given by

$$\mathbf{A}(\mathbf{r}, t) = \sum_k\left(\frac{4\pi c^2\,\hbar}{2\omega_k V_0}\right)\{a_k \exp(-i\omega_k t + i\mathbf{k}\cdot\mathbf{r}) + c.c.\}\,\hat{\varepsilon}, \qquad (8)$$

where $\omega_r = kc$, V_0 is the volume of the system and $\hat{\varepsilon}$ is the polarization vector which is taken the same for all plane waves. Only this simplest

case will be considered in this paper. The extension of the treatment given to more general situations is, however, straightforward Thus, considering that $H_{1R} = -\mathbf{d}_1 \cdot \mathbf{E}$ is the interaction between an electric dipole moment and an electric field, and remembering that $E = -(1/c)\,\partial \mathbf{A}/\partial t$ we obtain from equation (7):

$$dP_{if}^{IF} = \frac{2\pi\omega_k (N_k + 1)}{\hbar V_0} \left| \int_0^{t_0} dt \exp(-i\omega_k t) \langle \phi_F | \langle \psi_f | T^{\dagger}(t) \cdot \right.$$

$$\left. \cdot \mathbf{d}_1 \exp(i\mathbf{k} \cdot \mathbf{r}_1)\, T(t) | \psi_i \rangle | \phi_I \rangle \right|^2, \qquad (9)$$

where the time evolution operator T obeys now the equation $i\hbar \partial T(t, t')/\partial t = H,\ T(t, t')$, with H, $= H_0 +$ V.

Now we calculate the total average power emitted by the system with frequency between ω and $\omega + d\omega$ in the time interval t_0. Taking into account the density of final states of the emitted photons, summing over all directions of emission, multiplying by the energy of each photon and dividing by t_0, equation (9) becomes:

$$\frac{dP_{if}^{IF}}{t_0} = \frac{4\omega^4 N(\omega)\, d\omega}{3c^3} \frac{1}{2\pi t_0} \int_0^{t_0} dt \int_0^{t_0} dt' \exp[i\omega(t - t')] \cdot$$

$$\cdot \langle \phi_{I\,i} \quad |\theta^{\dagger}(t)| \psi_f \rangle | \phi_F \rangle \ \langle \phi_F | \langle \psi_f | \theta(t') |_{\mathbf{i}} \quad \phi_I \rangle, \qquad (10)$$

where $N(\omega)\, d\omega$ is the number of incident photons with frequency between ω and $\omega + d\omega$ (we assume $N(\omega)\, d\omega \gg 1$) and $\theta(t) = T^{\dagger}(t) \mathbf{d}_1 \exp(i\mathbf{k} \cdot \mathbf{r}_1) T(t)$.

Averaging equation (10) over all posible initial states and summing over all posible final states of the system, we obtain the emitted power $dI(\omega)/d\omega$:

$$dI(\omega)/d\omega = \frac{4\omega^4 N(\omega)}{3c^3} \cdot F(\omega), \qquad (11)$$

where the spectrum of the emitted or absorbed light $F(\omega)$ is given by:

$$F(\omega) = \frac{1}{2\pi t_0} \sum_r \sum_i \rho_i^{(1)} \rho_I \int_0^{t_0} dt' \int_0^{t_0} dt \exp[i\omega(t - t')] \cdot$$

$$\cdot \langle \phi_I | \langle \psi_i | \theta^{\dagger}(t) | \psi_f \rangle | \phi_F \rangle \cdot \langle \phi_F | \langle \psi_f | \theta(t') | \psi_i \rangle | \phi_I \rangle, \qquad (12)$$

where the density matrix $\rho_i^{(1)}$ is given by

$$\rho_i^{(1)} = \langle \psi_i | \exp(-\beta h^{(1)}) | \psi_i \rangle / Z_{\psi}$$

where $Z_\psi = \sum_n \langle \psi_n | \exp(-\beta h^{(1)}) | \psi_n \rangle$ is the partition function, $\beta = 1/(\kappa_B T)$, κ_B the Boltzmann constant and T the absolute temperature of the gas. The density matrix ρ_I is given by

$$\rho_I = \langle \phi_I | \exp[-\beta(H_0 + V - h^{(1)})] | \phi_I \rangle / Z_\phi ,$$

with $Z_\phi = \sum_m \langle \phi_m | \exp[-\beta(H_0 + V - h^{(1)}] | \phi_m \rangle$, assuming that the perturbation of the internal states $|\psi_i\rangle$ due to the interaction with the perturbing molecules can be neglected in the density matrix. This means that to write equation (12) we assume that the total matrix density operator $\rho = \exp[-\beta(H_0 + V)]/Z$ is diagonal in the energy representation $|\psi_n\rangle|\phi_m\rangle$. This approximation can be done in most cases since the perturbation of the states $|\psi_n\rangle$ is small[16]. So, equation (12) can be written in a simpler form:

$$F(\omega) = \frac{1}{2\pi t_0} \int_0^{t_0} dt' \int_0^{t_0} dt \exp[i\omega(t - t')] \, Tr[\rho \theta^\dagger(t) \cdot \theta(t')]. \tag{13}$$

In the limit of $t_0 \to \infty$, equation (13) becomes

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} ds \exp(ias) \, \phi(s) = \frac{1}{\pi} Re \int_0^{\infty} ds \exp(i\omega s) \, \phi(s), \tag{14}$$

where

$$\phi(s) = Tr[\rho \theta^\dagger \cdot \theta(s)] \tag{15}$$

and $\theta^\dagger \equiv \theta^\dagger(s = 0)$.

The time correlation function $\phi(s)$ can also be written as

$$\phi(s) = \sum_{if} \rho_i^{(1)} [\theta_{if}^\dagger \cdot \theta_{if}(s)]_{Av}, \tag{16}$$

where

$$[\theta_{if}^\dagger \cdot \theta_{if}(s)]_{Av} \equiv \sum_I \rho_I \langle \phi_I | \{ \langle \psi_i | \theta^\dagger | \psi_f \rangle \cdot \langle \psi_f | \theta(s) | \psi_i \rangle \} | \phi_I \rangle . \tag{17}$$

The natural lifetimes of the states have not been taken into account in the above expression. These can be easily introduced modifying slightly the theoretical approach[17]. In Sec. 3, these natural lifetimes will be considered

Up to now, we have considered only one emitting particle. However, to take into account $N^{(1)}$ radiating particles, it is enough to consider these particles in the Hamiltonian H, = H, + V.

The spectrum $F(\omega)$ defined by equations (14) and (15) gives the line shape of transitions taking into account both the Doppler effect and the perturbation of the internal energy levels which participate in the observed transitions. Our results can be applied to gases, liquids and solids. However, as will be seen in next section, these results will be applied only for gases in some special cases.

3. Gases

With our general equation (14), we shall study in this Section only gases in some particular conditions.

In gases, there are both the translational modes of the individual molecules and the collective motions of the molecules. We shall distinguish two limiting cases[18] : (1) when we can speak of individual molecule translation and (2) when we can speak of collective sound waves. The case (1) occurs when the de Broglie wave length h/p is smaller than the inter-molecular distance $(V_0/N)^{1/3}$ and the case (2) when $h/p \gg (V_0/N)^{1/3}$. If $h/p \sim (V_0/N)^{1/3}$ neither of the two concepts can be applied.

The case (2) will be considered in a forthcoming paper. In this paper only the limiting case (1) will be analysed: in this case we have the condition $p \gg h(N/V_0)^{1/3}$ that is satisfied for sufiiciently high temperatura and low pressures. This is a very simplifying hypothesis but nevertheless the analysis of the equation (16) is still tremendously difficult. The problem becomes a little less difficult if the following conditions are satisfied: (a) the probability of three particle collisions is negligible and (b) the ratio between the average duration of a collision and the average time between collisions is very small. When (a) and (b) are fulfilled, we have what is called "impact approximation"[8,11] .

We must note that the condition $p > h(N/V_0)^{1/3}$ guarantees the translational motion and $1/T_c \gg (N/V_0)\sigma\bar{v}$ the impact approximation[8], where $\bar{v}$ is the mean relative velocity between two particles, σ the collision cross-section and T_c the collision time.

It can be shown[19] that in the impact approximation the interaction energy between the molecules is negligible in comparison with their kinetic ener-

gies. This means that the system behaves as a perfect gas. In these conditions, the translational states of the molecules can be taken, as a very good zeroth-order approximation, as plane waves and the time evolution operator can be substituted by products of S matrices for collisions between two molecules.

In this case, the state of the emitting molecule is written as $|\Psi_1\rangle = |\alpha_1\rangle|\psi\rangle|\mathbf{p}_1\rangle$, where $\mathbf{p}_1$ is a plane wave and $|\alpha_1\rangle$ includes the remaining internal degrees of freedom. In these conditions, equation *(16)* becomes:

$$\phi(s) = \sum_{\psi_i\psi_f} \sum_{p_1\bar{p}_1} \rho_{p_1} \rho_i^{(1)} [\langle \psi_i \mathbf{p}_1 | \theta^\dagger | \psi_f \bar{\mathbf{p}}_1 \rangle \cdot \cdot \langle \psi_f \bar{\mathbf{p}}_1 | T^\dagger(s) \theta T(s) | \psi_i \mathbf{p}_1 \rangle]_{Av}, \qquad (18)$$

where the average $[\ldots]_{Av}$ is over the internal and translational states of the perturbing molecules and over the internal states $|\alpha_1\rangle$.

Introducing the projectors $\sum_{\psi' \bar{p}_1} |\psi' \mathbf{p}_1'\rangle \langle \mathbf{p}_1' \psi'|$ and $\sum_{\psi'' \bar{p}_1''} |\psi'' \mathbf{p}_1''\rangle \langle \mathbf{p}_1'' \psi''|$, equation (18) takes the form:

$$\phi(s) = \sum_{\substack{\psi_i\psi_f \\ p_1\bar{p}_1}} \sum_{\substack{\psi'\psi'' \\ p_1'p_1''}} \rho_{p_1} \rho_i^{(1)} [\langle \psi_i \mathbf{p}_1 | \theta^\dagger | \psi_f \bar{\mathbf{p}}_1 \rangle \cdot \cdot \langle \psi_f \bar{\mathbf{p}}_1 | T^\dagger(s) | \psi' \mathbf{p}_1' \rangle \langle \psi' \mathbf{p}_1' | \theta | \psi'' \mathbf{p}_1'' \rangle \langle \psi'' \mathbf{p}_1'' | T(s) | \psi_i \mathbf{p}_i \rangle]_{Av}. \qquad (19)$$

In the case of non-overlapping lines[8], we can replace

$$[\ldots]_{Av} \to [\ldots]_{Av} \cdot \delta_{\psi',\psi_f} \cdot \delta_{\psi'',\psi_i}$$

and observe in different intervals of frequencies different spectral lines due to the transitions $|\psi_i\rangle \to |\psi_f\rangle$. This means that the total spectrum $F(\omega)$ (see equation *(14)*) is given by the sum of independent contributions of all pair of states $|\psi_i\rangle$ and $|\psi_f\rangle$ that appear in equation *(19)*. So, in principle, it is enough to consider in this equation only one pair of states: one initial state $|\psi_i\rangle$ and one final state $|\psi_f\rangle$. In these conditions, equation *(19)* becomes, defining $U(s)$ as $T(s) = \exp\left[-\frac{is}{\hbar}(H_1 + H_r)\right] U(s)$:

$$\phi_{if}(s) = \rho_i^{(1)} \exp(-i\omega_{if} s) \sum_{p_1\bar{p}_1} \sum_{p_1'\bar{p}_1'} \exp[-is(p_1^2 - \bar{p}_1^2)/2m_1 A].$$

$$\cdot \rho_{p_1}^{(1)} [\langle \psi_i \mathbf{p}_1 | \theta^\dagger | \bar{\mathbf{p}}_1 \psi_f \rangle \cdot \langle \psi_f \mathbf{p}_1' | \theta | \mathbf{p}_1'' \psi_i \rangle \cdot \cdot \langle \psi_f \bar{\mathbf{p}}_1 | U^\dagger(s) | \mathbf{p}_1' \psi_f \rangle \langle \psi_i \mathbf{p}_1'' | U(s) | \mathbf{p}_1 \psi_i \rangle]_{Av}, \qquad (20)$$

where $\omega_{if} = (\varepsilon_i - \varepsilon_f)/\hbar$.

As will be seen in what follows, the reduction of the Doppler width is given essentially by the term $\langle \psi_i \mathbf{p}, | \theta^{\dagger} | \mathbf{p}_1 \psi_f \rangle \cdot \langle \psi_f \mathbf{p}_1' | \theta | \mathbf{p}_1'' \psi_i \rangle$ and the broadening and shift of the line due to the perturbation of the internal states given essentially by the term

$$\langle \psi_f \bar{\mathbf{p}}_1 | U^{\dagger}(s) | \mathbf{p}_1' \psi_f \rangle \langle \psi_i \mathbf{p}_1'' | U(s) | \mathbf{p}_1 \psi_i \rangle .$$

We see, however, from equation (20) that in the general case the contributions of both effects to the line shape are strongly correlated. Since the exact calculation of the correlation function $\phi_{if}(s)$ is extremely difficult, we shall study only three particular cases of $\phi_{if}(s)$: (a) when the perturbation of the states $|\psi_n\rangle$ is negligible, (b) when the Doppler effect is negligible and (c) when the perturbation of the internal states $|\psi_n\rangle$ and the reduction of the Doppler width are uncorrelated effects.

3a. Negligible Perturbation of the Internal States $|\psi_n\rangle$

In this case, the equation (20) can be written approximately, considering also the natural half-width γ_{if}, as:

$$\phi_{if}(s) = \rho_i^{(1)} \exp[-i\omega_{if} s - \gamma_{if} s] |\langle \psi_f | \bar{\mathbf{d}}_1 | \psi_i \rangle|^2 \cdot \cdot \langle \exp(-\mathrm{ik} \cdot \mathrm{r},) \exp(\mathrm{ik} \cdot \mathrm{r}, (s)) \rangle , \qquad (21)$$

where d, is the average dipole moment of the emitting molecule,

$$\langle \ldots \rangle = \sum_{\mathbf{p}_1} \rho_{\mathbf{p}_1}^{(1)} [\langle \mathbf{p}_1 | \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_1(s)) | \mathbf{p}_1 \rangle]_{av} , \qquad (22)$$

where the average $[\ldots]_{av}$ is only over the translational states of the perturbing molecules,

$$\exp(\mathrm{ik} \cdot \mathbf{r}_1(s)) = \exp(iH' s/\hbar) \exp(\mathrm{ik} \cdot \mathrm{r}_1) \exp(-iH' s/\hbar),$$

$$H' = T^{(1)} + \sum_{j=1}^{N(2)} T_j^{(2)} + \bar{V} ,$$

and $\bar{V}$ the interaction potential between the emitting and perturbing particles which is a function only of the distances between the interacting particles. The potential $\bar{V}$ is obtained averaging the potential V, defined in equation (1), over all internal states of the emitting and perturbing particles.

So, to obtain $\phi_{if}(s)$ it is enough to calculate the correlation function defined in equation (22). Taking k parallel to the x-axis, we can put equation (22) in a simpler form assuming that x_1 and $x_1(s)$ are random Gaussian variables[7]:

$$\langle \exp(-ikx_1) \exp(ikx_1) \rangle = \exp\left\{ -\frac{k^2}{2} \langle (x_1 - x_1(s))^2 \rangle + \right.$$

$$\left. + \frac{k^2}{2} [x_1, x_1(s)] \right\}. \qquad (23)$$

Assuming also that the classical treatment is sufficiently accurate to describe the motion, the condition $[x, , x_1(s)] = 0$ is satisfied. Since we assume that the recoil shift is negligible, this approximation is satisfied[7]. In this case, (22) becomes:

$$\langle \exp(-ikx_1) \exp(ikx_1(s)) \rangle = \exp\left[-\frac{k^2}{} \langle (x_1 - x, (s))^2 \rangle \right]. \qquad (24)$$

So, our problem is solved if the correlation function $\langle (x, -x_1(s))^2 \rangle$ is obtained. Since translational states of many particles are involved, this is a very difficult task. It would be easier if only collective motions (phonons) were present as occurs in solids[7].

The correlation function $\langle (x_1 - x_1(s))^2 \rangle$ has been obtained approximately in some different ways[6,7] but it will be calculated here with a new approach.

Indicating by τ the mean free time between strong collisions (hard sphere collisions) and T_c the collision time, with $\tau \gg T_c$, the particles can be wnsidered as free for most of the time. Observing the motion of the emitting particle, we see that it behaves as a free particle which is periodically disturbed, with period τ, by random collisions with perturbing molecules.

Let us now write the states of the emitting particle. Assuming that the fluid is contained in a cubic box of volume $V_0 = L^3$ we take the x-axis parallel to one edge of the cube and the origin at the middle point of L. After this, we divide L in N intervals of length 1, where λ is the mean free-path along the x-axis. This means that x goes from $-N\lambda/2$ to $N\lambda/2$.

The wave-function $|m\rangle$ of the emitting molecule in a k^{th} interval will be written as $|m) = \frac{1}{\sqrt{\lambda}} \exp\left[-i \left(\frac{2\pi m}{1} x + \theta_k \right) \right]$, where m is an integer and θ_k a phase of the state caracteristic of the k^{th} interval.

As one can easily verify, this wave function is symmetric at the endpoints $-[N-2(k-1)]\,\lambda/2$ and $-(N-2k)\,\lambda/2$ of the k^{th} interval.

With these wavefunctions the correlation function $\langle (x_1 - x_1(s))^2 \rangle$ becomes:

$$\langle (x_1 - x_1(s))^2 \rangle = 4 \sum_{mm'} \rho_m |(x_1)_{mm'}|^2 \sin^2 [(E_m - E_{m'})\, s/2\hbar], \qquad (25)$$

where $\rho_m = \frac{h}{\lambda} (\beta/2\pi\mu)^{1/2} \exp(-\beta E_m)$, $\mu = m_1 m_2/(m_1 + m_2)$ the reduced mass of the emitting and perturbing molecules, $E_m = \frac{m^2 h^2}{2pA^2}$ and

$$(x_1)_{mm'} = \frac{1}{\lambda} \int_{-\lambda/2}^{\lambda/2} dx_1\, x_1 \exp [-i\, 2\pi (m - m')\, x_1/\lambda].$$

In the limit of continuum states, equation (25) becomes, omitting the indices 1 for simplicity:

$$\langle (x - x(s))^2 \rangle = (16/h\lambda) \int_{-\infty}^{+\infty} dp\, \rho_p \int_{-\infty}^{+\infty} dp' \left(\frac{\hbar}{p - p'}\right)^4$$

$$\sin^2 [(p - p')\,(p + p')\, s/4\hbar\mu].$$

$$\cdot \left[\sin\left(\frac{p - p'}{2\hbar}\lambda\right) - \left(\frac{p - p'}{2\hbar}\lambda\right) \cos\left(\frac{p - p'}{2\hbar}\lambda\right)\right]^2$$

where p and p' are relative momenta, between emitting and perturbing molecules, along the x-axis and ρ_p is the density matrix in the momenta space. Putting

$$\sin^2 [(p - p')\,(p + p')\, s/4\hbar\mu] \cong \sin^2 [(p - p')\, ps/2\hbar\mu]$$

and defining the variable $\chi = (p - p')\, p/\hbar\mu$, we obtain:

$$\langle (x - x(s))^2 \rangle = (16/\pi\lambda) \int_0^\infty d\chi \left[\frac{1}{\chi} \sin (\chi\, s/2)\right]^2 \int_0^\infty dv\, \rho_v\, v^3 \cdot$$

$$[\sin \left(\frac{\chi}{2v} A\right) - (\lambda/2v) \cos\left(\frac{\chi}{2v} A\right)]^2,$$

where ρ_v is the density matrix in the velocity space. As can be easily verified this equation can be written approximately as

$$\langle (x - x(s))^2 \rangle \cong (16\, u_x/\lambda\pi) \int_0^\infty d\chi \left[\frac{1}{\chi} \sin(\chi\, s/2)\right]^2 \cdot \left[\frac{u_x}{\chi} \sin(\chi\, \lambda/2\, u_x)\right]^2$$

$$= (2\, u_x^2/\pi) \int_0^\infty d\theta \left(\frac{\sin\hat{\theta}}{\theta}\right)^2 \left[\frac{\tau}{\theta} \sin(\theta s/\tau)\right]^2, \tag{27}$$

where $u_x = (2\kappa_B T/\pi\,\mu)^{1/2}$ is the mean value of the modulus of the x-component of the relative velocity and $\tau \cong \lambda/u_x$ r $\bar{\lambda}/\bar{v}$ where $\bar{\lambda}$ is the mean free path and $\bar{v} = \left(\frac{8\,\kappa_B T}{\pi\,\mu}\right)^{1/2}$ is the mean relative velocity.

We shall consider now two particular cases of the equation *(27)*: when the emitting particle collides many times during the natural lifetime of the level and when no collisions occur during the lifetime.

Let us see then what happens when the emitting particle collides many times during the lifetime $1/\gamma$ of the state. This means that $1/\gamma \gg \tau$. This is equivalent to assume in the equation *(27)* the limit $s/\tau \gg 1$ in the function $\left[\frac{\sin(\theta s/\tau)}{\theta/\tau}\right]$ which can be considered different from zero only in the interval between 0 and $\pi\,\tau/s$. Since in this interval the function $(\sin^2\theta)/\theta^2$ can be taken equal to *1*, we obtain:

$$\langle (x_1 - x_1(s))^2 \rangle \cong 2\, u_x^2\, \tau\, s = 2\, D\, s, \tag{28}$$

where $D = u_x^2\, \tau$ r $\frac{\nabla}{3}\bar{\lambda}$ is the diffusion coefficient.

In this case, equation *(21)* becomes, using equations *(24)* and *(28)*:

$$\phi_{if}(s) = |\langle \psi_f | \bar{\mathbf{d}}_1 | \psi_i \rangle|^2 \exp[-is(\omega_{if} - i\,\gamma_{if} - i\,k^2\, D)],$$

which will give the line shape $F(\omega)$, defined by equation *(14)*:

$$F(\omega) = \frac{1}{\pi} |\langle \psi_f | \bar{\mathbf{d}}_1 | \psi_i \rangle|^2 \frac{(\gamma_{if} + \omega^2\, D/c^2)}{(\omega - \omega_{if})^2 + (\gamma_{if} + \omega^2\, D/c^2)^2}.$$

Since the diffusion coefficient $D = \frac{\bar{v}}{3}\bar{\lambda} \propto \frac{1}{P}$, where P is the pressure of the gas of perturbing molecules, we see that when P increases the half-width decreases. This is the Mossbauer Effect in gases or Dicke Effect[6,7]. We must observe that the Doppler contribution $\frac{\omega^2}{c^2} D$ to the width, for a given pressure, becomes bigger when the frequency ω of the emitted photon increases. This is essentially the effect of the recoil of the emitting molecule in the emission of a photon with frequency ω.

For high pressures, when the three particle collisions are as frequent as the two particle collisions, the impact approximation is not satisfied. In this case the result seen in equation (28) is not valid and another approximation mus be used to calculate $\langle (x - x(s))^2 \rangle$.

Let us now see what happens if during the lifetime $1/\gamma$ the emitting particle does not collide. This means that $\tau \gg 1/\gamma$, which occurs, for instance, when the pressure is so small that the particle is practically free during the lifetime $1/\gamma$. In these conditions, the contribution of $\langle (x - x(s))^2 \rangle$ can be calculated taking the limit $\tau \to \infty$:

$$\lim_{\tau \to \infty} \langle (x - x(s))^2 \rangle = \frac{2 u_x^2}{\pi} \int_0^\infty d\theta \left(\frac{\sin \theta}{\theta} \right)^2 \lim_{\tau \to \infty} \left(\frac{\sin(\theta s/\tau)}{\theta s/\tau} \right]^2 s^2$$

$$= (u_x s)^2 = (\bar{v} s)^2/3. \qquad (29)$$

In this case, the line shape $F(\omega)$ defined in equation (14) becomes, using (22), (24) and (29):

$$F(\omega) \cong \frac{c}{2\omega} \left(\frac{\mu}{\kappa_B T} \right)^{1/2} \exp \left[- \left(\frac{\omega - \omega_{if}}{\omega} \right)^2 \frac{\pi \mu c^2}{4 \kappa_B T} \right],$$

which is, approximately, a Gaussian with half-width

$$\Delta\omega'_{if} \cong \frac{c}{\omega_{if}} \left(\frac{2 \kappa_B T}{\pi \mu} \right)^{1/2}$$

In the particular case of self-perturbations, the half-width is given by

$$\Delta\omega'_{if} \cong \frac{c}{\omega_{if}} \left(\frac{4 \kappa_B T}{\pi m_1} \right)^{1/2}.$$

3b. **Negligible** Doppler Effect

If the Doppler effect is negligible, we can put $k = 0$ in $\theta = \mathbf{d}_1 \exp(ik \cdot r,)$. Thus, equation (20) becomes:

$$\begin{aligned}\phi_{if}(s) &= \rho_i^{(1)} \exp(-i\omega_{if} s) \sum_{p_1 p_2} \rho_{p_1}^{(1)} \rho_{p_2}^{(1)} [|\langle\psi_f|\mathbf{d}_1|\psi_i\rangle|^2 \cdot \\ &\quad \cdot \langle \mathbf{p}_1|\langle \mathbf{p}_2|\{\langle\psi_f|U^\dagger(s)|\psi_f\rangle\langle\psi_i|U(s)|\psi_i\rangle\}|\mathbf{p}_1\rangle|\mathbf{p}_2\rangle]_{Av} \\ &\cong \rho_i^{(1)} \exp(-i\omega_{if} s)|\langle\psi_f|\bar{\mathbf{d}}_1|\psi_i\rangle|^2 \sum_{p_1 p_2} \rho_{p_1}^{(1} \rho_{p_2}^{(2)} \cdot \\ &\quad \cdot \langle \mathbf{p}_1|\langle \mathbf{p}_2|[\langle\psi_f|U^\dagger(s)|\psi_f\rangle\langle\psi_i|U(s)|\psi_i\rangle]_{Av}|\mathbf{p}_1\rangle|\mathbf{p}_2\rangle \qquad (30)\end{aligned}$$

where $\mathbf{d}_1$ is the average dipole moment of the emitting particle, $\mathbf{p}_2$ the linear momentum of the perturbing molecule and the average $[\ldots]_{Av}$ means an average only over the internal states of the perturbing molecules and the states $|\alpha_1\rangle$ of the emitting one.

Using the relative momentum $|q) = h^{-3/2} \exp(iq \cdot R/\hbar)$ between the emitting and perturbing particles, where R is the relative distance between them, equation (30) takes the form:

$$\begin{aligned}\phi_{if}(s) &= \rho_i^{(1)} \exp(-i\omega_{if} s)|\langle\psi_f|\bar{\mathbf{d}}_1|\psi_i\rangle|^2 \cdot \\ &\quad \sum_q \rho_q \langle \mathbf{q}|[\langle\psi_f|U^\dagger(s)|\psi_f\rangle\langle\psi_i|U(s)|\psi_i\rangle]_{Av}|\mathbf{q}\rangle \cdot\end{aligned}$$

In the impact approximation [7,8] it becomes

$$\phi_{if}(s) = \rho_i^{(1)}|\langle\psi_f|\bar{\mathbf{d}}_1|\psi_i\rangle|^2 \exp[-is(\omega_{if} + S''_{if} - i\Delta\omega''_{if})]$$

where the shift S''_{if} and the half-width $\Delta\omega''_{if}$ are linearly proportional to the pressure P. In fig. 1 of reference (12), the half-width due to the perturbation of the internal energy levels is represented by a dashed line.

A typical behaviour[20] of the line width as function of P is shown in fig. 1[12], in which we consider the pressure axis divided in three regions. In region 1, the perturbation effect of the collisions on the internal states of the emitting molecules is very small. The effect of collisions in this region is practically a reduction of the Doppler width only. In region 2, Aw is almost independent of P and reaches its minimum value. In region 3, Ao depends linearly on P. In this region the Dicke effect is negligible, and we may consider only the perturbations of the internal energy levels.

The line shift, within the experimental error, is always proportional to P[21,23]. As will be shown below, our theoretical predictions agree with these experimental results.

3c. **Uncorrelated Contributions** of **the** Dicke Effect and of the Perturbations of the **Internal** Energy **Levels**

Since $\mathbf{p}_1 - \bar{\mathbf{p}}_1 = \hbar\,\mathbf{k} = \mathbf{p}_1'' - \mathbf{p}_1'$, equation (20) can be wntten as

$$\phi_{if}(s) = \rho_i^{(1)} \exp(-i\,\omega_{if}\,s) \sum_{\substack{p_1\,\bar{p}_1 \\ p_1'\,p_1''}} \rho_{p_1}^{(1)} [\langle\psi_i|\langle\mathbf{p}_1|\theta^{\dagger}|\bar{\mathbf{p}}_1\rangle|\psi_f\rangle \cdot$$
$$\cdot \langle\psi_f|\langle\bar{\mathbf{p}}_1|\exp(is\,\bar{p}_1^2/2\,m_1\,\hbar)\;\theta\;\exp(-is\,p_1^2/2\,m_1\,\hbar)|\mathbf{p}_1\rangle|\psi_f\rangle \cdot$$
$$\cdot \langle\psi_f|\langle\mathbf{p}_1 - \hbar\,\mathbf{k}|\,U^{\dagger}(s)\,|\mathbf{p}_1'\rangle|\psi_f\rangle\langle\psi_i|\langle\mathbf{p}_1' + \hbar\,\mathbf{k}|\,U(s)\,|\mathbf{p}_1\rangle|\psi_i\rangle]_{Av}$$

that becomes, remembering that in the **impact** approximation the **interaction** energy $V(R)$ of the emitting particle with the perturbing **ones is** negligible **in comparison** with the kinetic **energies** of the particles and that θ depends only of the emitting particle,

$$\phi_{if}(s) = \rho_i^{(1)} \exp(-i\,\omega_{if}\,s)\,|\langle\psi_f|\,\bar{\mathbf{d}}_1\,|\psi_i\rangle|^2 \cdot \sum_{p_1\,\bar{p}_1\,p_1'} \rho_{p_1}^{(1)} \cdot$$
$$\cdot [\langle\mathbf{p}_1|\exp(-i\,\mathbf{k}\cdot\mathbf{r}_1)|\bar{\mathbf{p}}_1\rangle\langle\bar{\mathbf{p}}_1|\exp(i\,\mathbf{k}\cdot\mathbf{r}_1(s))|\mathbf{p}_1\rangle]_{av} \cdot$$
$$\cdot [\langle\psi_f|\langle\mathbf{p}_1 - \hbar\,\mathbf{k}|\,U^{\dagger}(s)\,|\mathbf{p}_1'\rangle|\psi_f\rangle\langle\psi_i|\langle\mathbf{p}_1' + \hbar\,\mathbf{k}|\,U(s)\,|\mathbf{p}_1\rangle|\psi_i\rangle]_{Av}$$

where the average $[\ldots]_{av}$ **is** only over the translational states of the **perturbing** molecules, $\exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}_1(s)) = \exp(i\,\mathrm{H}'\,s/\hbar)\,.\,\exp(\mathrm{i}\,\mathbf{k}\,.\,\mathrm{r},)\,\exp(-\mathrm{i}\,\mathrm{H}'\,s/\hbar)$ and $\mathrm{H}' = T^{(1)} + \sum_{j=1}^{N(2)} T_j^{(2)} + \bar{V}$. **Assuming** that the momentum $|\mathrm{h\,k}|$ **is much** smaller than the average momentum of the molecules, we have:

$$\phi_{if}(s) = \rho_i^{(1)}\,|\langle\psi_f|\,\bar{\mathbf{d}}_1\,|\psi_i\rangle|^2 \exp(-i\,\omega_{if}\,s) \cdot$$
$$\cdot \sum_{p_1} \rho_{p_1}^{(1)} [\langle\mathbf{p}_1|\exp(-i\,\mathbf{k}\cdot\mathbf{r}_1)\exp(i\,\mathbf{k}\cdot\mathbf{r}_1(s))|\mathbf{p}_1\rangle]_{av} \cdot$$
$$\cdot [\langle\mathbf{p}_1|\langle\psi_f|\,U^{\dagger}(s)\,|\psi_f\rangle\langle\psi_i|\,U(s)|\psi_i\rangle|\mathbf{p}_1\rangle]_{Av}. \qquad (31)$$

As we have **seen** in (3.a) and **(3.b),** the Dicke effect and the **perturbation** of the **internal** energy levels are **given** essentially by the factors $[\ldots]_{av}$ and $[\ldots]_{Av}$, respectively.

Since the factor $[\ldots]_{av}$ **is** real (r, and $\mathbf{r}_1(s)$ commute), it does not **contribute** to the shift. The other factor $[\ldots]_{Av}$ predicts a line shift linearly **proportional** to the pressure, in agreement with the experimental results.

The shift and width of the line due to the perturbation of the internal energy levels in the impact approximation depends only on the number of collisions per unit time. This means that it depends on the density of perturbing molecules and on the relative velocity between the emitting and perturbing particles. It does not depend on the translational motion of the emitting molecule as occurs with the Dicke Effect. The same shift and width obtained with an emitting particle in motion can be obtained with this particle at rest.

If therefore $m_1 \gg m_2$, the emitting particle in the bracket $[\ldots]_{Av}$ can be taken as at rest since the average relative velocity $\bar{v} = (8\,\kappa_B T/\pi\,\mu)^{1/2} \cong$ $\cong (8\,\kappa_B T/\pi\,m_2)^{1/2} = \bar{v}_2$. Thus, equation (31) becomes:

$$\phi_{if}(s) = \rho_i^{(1)} |\langle \psi_f | \bar{\mathbf{d}}_1 | \psi_i \rangle|^2 \langle \exp(-i\,\mathbf{k}\cdot\mathbf{r}_1) \exp(i\,\mathbf{k}\cdot\mathbf{r}_1(s)) \rangle \cdot$$
$$\cdot \exp[-is(\omega_{if} + S''_{if} - i\,\Delta\omega''_{if})] =$$
$$= \rho_i^{(1)} |\langle \psi_f | \bar{\mathbf{d}}_1 | \psi_i \rangle|^2 \exp\{-is[\omega_{if} + S''_{if} - i(\Delta\omega'_{if} + \Delta\omega''_{if})]\},$$

where $\Delta\omega'_{if}$ is due to the Dicke effect and S''_{if} and $\Delta\omega''_{if}$ to the perturbation of the internal states, according to the convention adopted in Secs. (3.a) and (3.b). The shift S''_{if} and the half-width $\Delta\omega''_{if}$ are calculated putting $\bar{v} = \bar{v}_2$.

In this approximation therefore, the reduction of the Doppler width and the perturbation of the internal energy levels are uncorrelated effects. The total half-width $\Delta\omega_{if}$ is given by $\Delta\omega_{if} = \Delta\omega'_{if} + \Delta\omega''_{if}$. This particular case is illustrated in fig. 1 of Ref. (12).

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