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Effect of collisions on spectral lines in gases

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Abstract. Collisions between an emitter and the surrounding buffer gas particles influence the emission lines. A collision may perturb the emitter in its excited and ground states, cause direct transitions between the levels, and at the same time, change the velocity of the emitter. In this paper, we present a model which deals for the first time with all these effects when they occur *simultaneously* in each collision. The model assumes the emitter to be subject to random collisions by the surrounding gas particles which are taken to constitute a heat bath in thermal equilibrium. The collisions are assumed to be binary, instantaneous, and to occur with a probabiity given by the Poisson distribution. These assumptions are shown to be equivalent to the widely used impact approximation in the collision broadening theory. We discuss several special cases of the general result for the line shape obtained in the paper.

Keywords. Spectral line shape; collision broadening; impact approximation; frequency modulation; phase modulation; velocity modulation.

1. Introduction

The subject of spectral line shapes in gases under the influence of pressure and temperature is an old and important one with applications to astrophysics, plasma physics, laser physics, and other branches of atomic and molecular spectroscopy. The phenomenon is generally known as the collision or the pressure broadening of spectra. Qualitatively speaking, a change in pressure (or temperature) of the gas alters the mean free time of collisions between gaseous atoms or molecules. This makes the lines undergo modulations in the form of broadening, shift, narrowing, etc.

Following the pioneering work by Anderson (1949) and Baranger (1958a, b, c), the subject of collision broadening has been thoroughly studied including complete quantum mechanical treatments of the radiating system and its perturbers. A significant advance in the theory has been the introduction by Fano (1963) of the concepts of irreversible statistical mechanics. In this, the radiating system is assumed to be imbedded in a large heat bath consisting of the surrounding particles. The spectral line shape is then given in terms of a relaxation matrix for the radiating system in which the degrees of freedom of the surrounding heat bath are suitably averaged over. Fano and several other authors have presented calculations involving systematic expansion of the relaxation matrix in terms of the density of the perturbers. Instead of giving a detailed review of the existing literature, we draw the attention of

the reader to the numerous references contained in the recent paper by Davies (1975) for a bibliography on the subject.

Whereas collision broadening is commonly regarded as an effect which arises from simultaneous perturbations of the upper and the lower levels of a transition due to the interaction between the system and the perturbers during collisions, there is another source of broadening, namely the Doppler broadening owing to the thermal velocity of the radiating system. In most calculations, the Doppler broadening is added separately to the contribution of the interaction. This procedure however relies on the assumption that a collision does not change the velocity of the radiating system which is of course not strictly correct, especially when the emitter is lighter than the perturber. In fact, a change in the velocity of the emitter can cause an appreciable reduction in the Doppler broadening contribution (Ben-Reuven 1969).

Despite the enormous activity in the subject over the last few decades, the interest in the question as to what happens when the same collision is responsible for both changes in velocity and nature of interaction, is relatively recent (see for example, Ben-Reuven 1975 and other references cited therein). It is this aspect of the problem which we examine more carefully in this paper. To simplify the mathematical treatment we consider the case of the emitter embedded in a foreign buffer gas of low density in which binary collisions alone are important. We also assume the collisions to be instantaneous. Our approach to the problem is based on the physical idea put forward by Fano (1963) in which the buffer gas is assumed to act like a heat bath with a large number of degrees of freedom. However, unlike Fano and others (Ben-Reuven 1966) who treat the interaction between the emitter and the surrounding bath on an *ab-initio* basis, we do not specifiy the exact nature of this interaction. Instead, it is recognised that the effect of the bath is to cause random changes in the velocities and the energy levels of the emitter. The formulation of the problem is thus closer in spirit to the stochastic theory models used extensively in other line shape problems (see for example, Clauser and Blume 1971).

In section 2 we present the theoretical formulation of the problem and introduce the different effects of a collision that are to be studied. The stochastic model and its mathematical solution are presented in section 3. The model is shown to be capable of describing the various effects of a collision in a rather simple mathematical manner. The relationship of the present work to other models which deal solely with the interaction effects is pointed out in section 4. The effect of velocity changing collisions is then introduced in section 5 and is illustrated in the strong collision model (Rautian and Sobel'man 1967) in which the emitter is supposed to be much lighter than the perturber. Finally, in section 6, we present some conclusions. The theoretical results obtained in this paper have implications in various spectroscopy experiments in gases. Here we shall not dwell on individual applications.

2. Theoretical formulation

The spectral line shape is given by the real part of (the analytic continuation to $s=-i\omega$ of) the Laplace transform of a correlation function (Ben-Reuven 1966):

$$I(s)=\mathrm{Re}\int_0^\infty dt\,\exp(-st)\,\mathrm{Tr}\left\{\rho d^\dagger(t)\exp[-i\mathbf{k}\cdot\mathbf{r}(t)]\,d(0)\exp[i\mathbf{k}\cdot\mathbf{r}(0)]\right\} \quad (1)$$

where ρ is the density matrix of the entire system (consisting of the emitter and its surroundings) governed by the Hamiltonian $\mathcal{H}$:

$$\rho=\exp(-\beta\mathcal{H})/\mathrm{Tr}\,[\exp(-\beta\mathcal{H}]),\ \beta=(K_BT)^{-1}, \tag{2}$$

d is the dipole operator responsible for the transition, **k** the wave vector of the emitted photon and **r** the centre of mass of the emitter. In eq. (1) the polarization effects are neglected. The time dependence of the operator $d^\dagger$ (or the operator **r**) is given in the Heisenberg picture by

$$d^\dagger(t)=\exp(i\mathcal{H}t)\ d\mathcal{H}^\dagger(0)\exp(-i\mathcal{H}t)=\exp(i\mathcal{H}^\times t)\ d^\dagger(0), \tag{3}$$

where $\mathcal{H}^\times$ is the Liouville operator associated with $\mathcal{H}$. (For properties of the Liouville operator to be used in this paper (see Blume 1968).

In this paper, we treat the variable **r** classically. So eq. (1) may be written

$$I(s)=\mathrm{Re}\int_0^\infty dt\,\exp(-st)\,\mathrm{Tr}\,(\rho d^\dagger(t)\,d(0)\exp[(-ik)\int_0^t v(t')\,dt')], \tag{4}$$

where v is the component of the velocity vector of the emitter in the direction of **k**.

The evaluation of the statistical average in (4) over the degrees of freedom of the emitter and its surroundings is a complicated many body problem. A standard scheme is to develop a perturbation theory for the time development operator in which some terms in the interaction are assumed small. In this paper, a different approach to the problem is presented. We adopt a physical picture in which the emitter is taken to be a small system surrounded by a heat bath with a large number of degrees of freedom representing the ensemble of the perturbers. The effect of the interactions between the emitter and the perturbers is assumed to make the velocity and the Hamiltonian of the emitter random functions of time. Such an attack to the problem is of course quite familiar in the theory of the Brownian motion.

As in the usual many body calculations (Fano 1963, Ben-Reuven 1966) the coupling of the emitter to the heat bath is assumed to be small compared to K_BT, where K_B is the Boltzmann constant and T the temperature. The average in (4), therefore, breaks up into two parts, one over the quantum mechanical states of the emitter (denoted by $\mathrm{Tr}_e\{\rho_e\ldots\}$), and the other over some stochastic variables which represent the degrees of freedom of the heat bath. Further, in this stochastic approach the Hamiltonian of the emitter $\mathcal{H}_e(t)$ is an explicit function of time. Equation (4) can thus be written

$$I(s)=\mathrm{Re}\int_0^\infty dt\exp(-st)\mathrm{Tr}_e\{\rho_e\langle\exp_T[i\int_0^t dt'(\mathcal{H}_e^\times(t')-kv(t'))]\rangle d^\dagger(0)d(0)\}, \tag{5}$$

where $\exp_T(\ldots)$ denotes a suitable time-ordering of the operators (since $[\mathcal{H}_e(t), \mathcal{H}_e(t')\neq 0$, in general), and $\langle\ldots\rangle$ denotes an average over the stochastic degrees of freedom (the meaning of the latter is explained below). A few comments are now in order regarding the roles of the different dynamical variables appearing in eq. (5). The

motion of the emitter can be separated into two parts: (i) motion of its centre of mass and (ii) motion of its constituents about the centre of mass. The former is described by the velocity variable while the latter is represented by some internal quantum numbers e.g., orbital and spin angular momenta, parity, etc. These latter degrees of freedom are the ones which give rise to quantised energy levels of the emitter that are described by the Hamiltonian $\mathcal{H}_e$.

To illustrate the type of situation we want to describe theoretically, let us represent the two levels involved in the transition by an effective spin-Hamiltonian

$$\mathcal{H}_e(t) = \bar{\omega} S_Z, \tag{6}$$

where $S=\frac{1}{2}$ so that S_Z can take up two values $\pm\frac{1}{2}$ and $\bar{\omega}$ measures the splitting between the two levels. In the model treated here, the radiating system is assumed to be in thermal equilibrium with the perturbers (foreign gas particles). The velocity distribution of the particles (including the emitter) is taken to be Maxwellian. Collisions between the emitter and the perturbers are assumed to be instantaneous as in the impact approximation (Baranger 1958a, b, c) and to be occurring at a rate governed by the mean free path of the perturbers. Each such collision can have the following three effects on the emitter.

(i) The emission spectrum may consist of several lines originating from a completely or partially lifted degeneracy of the energy levels involved in the transition. An example of the latter in atomic spectroscopy is the case where there is a spin-orbit interaction. The interaction between the emitter and a perturber during a collision modulates the wave function of the former in its excited and ground states. This makes the frequencies of transitions randomly time dependent. For example, in the case of a spin-orbit interaction, a collision may abruptly change either the spin or the orbit quantum numbers. The effect can be taken into account by writing (6) as

$$\mathcal{H}_e(t)=\omega(t)S_Z, \tag{7}$$

where $\omega(t)$ is a random function of time. A specific model for this random frequency modulation is discussed below.

(ii) At any instant the velocity of the emitter is governed by a Maxwellian probability distribution. A possible effect of a collision is to change the velocity of the emitter from one value to another.

(iii) Finally, a collision can induce a direct (in-elastic) transition between the two levels. To illustrate, if the perturber is electrically charged, it may give rise to a 'pulse' of an electric field as it collides with the emitter. This electric field then couples directly with the dipole moment of the emitter (the Stark effect). In this model where the energy levels are represented by a fictitious spin-Hamiltonian and the collisions are assumed to be instantaneous, such an additional term in the Hamiltonian may be included in (7) by writing

$$\mathcal{H}_e(t)=\omega(t)S_Z+\sum_{i=1}^{n}(\mathbf{S}\cdot\mathbf{h}_i)\delta(t-t_i), \tag{8}$$

where t_i ($i=1, 2, \ldots, n$) denote the instants when collisions occur and $\mathbf{h}_i$ is an effective field the emitter experiences during a collision. This additional term which contains

the raising and lowering operators S_+ and S_- can cause transitions between the states of the system which are taken to be the eigenstates of S_Z (cf. eqs (6) and (7)). Thus for example, if the wavefunction immediately prior to a collision is $|+\rangle$, the collision changes it to $C_+|+\rangle+C_-|-\rangle$, where the phase factors C_+ and C_- are assumed to be random. The second term on the right of eq. (8) can therefore be viewed as causing random phase modulations of the emitter which is a purely quantum mechanical effect.

3. Mathematical solution

We divide the time interval 0 to t into $(n+1)$ parts $t_1, t_2, \ldots t_n$ at which points collisions occur. Each collision is assumed to have a finite probability of changing the frequency and the velocity of the system and inducing a direct transition between the levels. We denote

$$U(t)=\exp_T\left[i\int_0^t dt'(\mathcal{H}_e^{\times}(t')-kv(t'))\right], \tag{9}$$

where the super operator $U(t)$ describes the time development of the system.

In the model presented here, we regard $U(t)$ as a matrix $\mathcal{U}(t)$ in a linear vector space spanned by an orthonormal set $\{|a, v)\}$ where the a's are *discrete* indices denoting the possible values of the frequency, and the v's are *continuous* states representing the allowed velocities of the emitter. While the same basic mechanism, namely a collision with a perturber, is responsible for both frequency and velocity modulations of the emitter, we recognise that frequency modulation arises from the interaction between the perturber and the emitter during a collision whereas velocity modulation is due solely to momentum imparted by the former on the latter. This means that frequency and velocity modulations may be assumed to be essentially uncorrelated albeit the cause for both events is the same. To illustrate, suppose the emitter is much heavier than the perturber. In that case, only a very little velocity-change is expected to occur due to a collision (a purely kinematic effect); on the other hand, the frequency-change may be quite substantial depending on the strength of the interaction. Therefore, the vector space at hand may be taken to be a product of two spaces, one discrete, the other continuous:

$$|av)=|a)|v). \tag{10}$$

Of course, we have to deal with yet another set of states, namely the quantum states of the emitter which are taken to be the eigenstates of the effective spin $\frac{1}{2}$ operator S_Z. Transitions between such states induce phase modulation which is also assumed to be independent of frequency and velocity modulation effects.

With these physical assumptions, the matrix $\mathcal{U}(t)$ can be constructed as

$$\begin{aligned}\mathcal{U}(t)=&\exp[i(\mathcal{H}_0^{\times}-kV)]t_1\,\mathcal{T}\exp i\,(\mathcal{H}_0^{\times}-kV)(t_2-t_1)\mathcal{T}\ldots\\ &\mathcal{T}\exp i\,(\mathcal{H}_0^{\times}-kV)(t-t_n),\end{aligned} \tag{11}$$

where, in accordance with eq. (7), we set

$$\mathcal{H}_0^{\times}=S_Z^{\times}\sum_{j=1}^{r}\omega_j F_j. \tag{12}$$

The frequencies ω_j may be written (cf., eq. (6))

$$\omega_j=\bar{\omega}+\triangle\omega_j, \tag{13}$$

where $\triangle\omega_j$ is a set of r possible frequencies of transitions which can occur because of perturbations of the emitter in its excited and ground states. Without any loss of generality, we can set

$$\sum_{j=1}^{r}\triangle\omega_j=0. \tag{14}$$

The F_j is an $r\times r$ matrix in the space spanned by the states $|\,a)$ and its matrix elements can be constructed as

$$(a\,|\,F_j\,|\,b)=\delta_{aj}\delta_{ab}. \tag{15}$$

The Liouville operator $\mathcal{H}_0^{\times}$ is a matrix in the combined space of the states $|\,a)$ and the quantum states $|-\rangle$ (the excited level) and $|+\rangle$ (the ground level). Following the notation used by Blume (1968) for the states of a Liouville operator, the element of $\mathcal{H}_0^{\times}$ within the quantum space is given by

$$(-+\,|\,\mathcal{H}_0^{\times}\,|\,--+)=-\sum_{j=1}^{r}\omega_j F_j. \tag{16}$$

The right hand side of eq. (16) is itself a matrix in the $|\,a)$-space. It is diagonal (cf. eq. (15)) with elements equal to the allowed frequencies of the system. The role of the F_j matrix is therefore merely to ' project ' out one of the r discrete frequencies that are possible in the emission spectrum.

Similarly, the velocity matrix V can be constructed in the continuous basis as

$$(v_0\,|\,V\,|\,v_1)=v_0\delta(v_0-v_2). \tag{17}$$

The $\mathcal{T}$-matrix is a collision operator or a transition matrix which plays the central role in the theory as it describes the entire dynamics of the system. Since the frequency, phase and velocity modulations are assumed to be independent of each other (although they occur in the same collision), the $\mathcal{T}$-matrix can be written as the product of three matrices

$$\mathcal{T}=\mathcal{T}_1\mathcal{T}_2\mathcal{T}_3, \tag{18}$$

where $(a\,|\,\mathcal{T}_1\,|\,b)$ and $(v_i\,|\,\mathcal{T}_2\,|\,v_f)$ are the respective probabilities that a collision changes (instantaneously) the frequency of the system from ω_a to ω_b and its velocity

from v_i to v_f, and $\mathcal{T}_3$ is a transition operator which, because of the interaction between the emitter and the perturber during a collision, can induce direct quantum transitions between the two levels of the emitter. In accordance with eq. (8),

$$\mathcal{T}_3 = \exp\,(i\mathbf{h}_i\cdot\mathbf{S}^{\times})_{\mathrm{av}}, \tag{19}$$

where $(\ldots)_{\mathrm{av}}$ denotes an average over the type of the pulse $\mathbf{h}_i$ the emitter experiences at the time t_i. Similar cases in which the collision operator has multiple effects have been studied in other line shape problems (Dattagupta and Blume 1974b, Dattagupta 1975, 1976).

A few remarks are to be made regarding the interpretation of eq. (19). Each collision, in at least so far as causing direct transitions between the two levels, is assumed to have an averaged effect only. This means that the fields $\mathbf{h}_i$ are taken to be uncorrelated from one collision to the next. Further, since the interaction $\mathbf{h}_i\cdot\mathbf{S}$ is Hermitian, the transitions induced by it between the eigenstates of S_Z are equally probable in either direction. This is valid when the level splitting $\bar{\omega}$ is much smaller than the thermal energy K_BT. The finite temperature effects can be taken into account by allowing in the model non-Hermitian terms in the Hamiltonian and to provide detailed balance (see for example, Clauser and Blume 1971).

To gain an understanding of the physical meaning of eq. (11), it is helpful to consider the matrix element of $\mathcal{U}(t)$ in the mixed $\{|\mathrm{av})\}$-space. It is given, from (12) - (19) by

$$\begin{aligned}(av_0\,|\,\mathcal{U}(t)\,|\,bv_1) = \sum_{cd\ldots}\int dv_2 dv_3 \ldots \exp[i(\omega_a S_Z^{\times} - kv_0)t_1](av_0\,|\,\mathcal{T}_1\,\mathcal{T}_2\,|\,cv_2)\mathcal{T}_3\\ \times\exp[i(\omega_c S_Z^{\times} - kv_2)\,(t_2-t_1)]\ldots(dv_3\,|\,\mathcal{T}_1\mathcal{T}_2\,|\,bv_1)\mathcal{T}_3\\ \times\exp[i(\omega_b S_Z^{\times} - kv_1)(t-t_n)].\end{aligned} \tag{20}$$

Equation (20) has the following interpretation. At $t=0$, the velocity of the emitter is v_0 and the splitting between the levels is ω_a. The emitter remains in this state until t_i when it encounters a collision. The collision has a probability $(av_0\,|\,\mathcal{T}_1\mathcal{T}_2\,|\,cv_2)$ of changing the splitting to ω_c and the velocity to v_2, and a certain probability of changing the quantum states of the emitter via $\mathcal{T}_3$. The emitter remains in this state until t_2 at which point another collision changes its state, and so on. Since all possible intermediate states have to be considered, we sum over the variables c, d,... and integrate over the velocities v_2, v_3...

The average required in eq. (5) is given by

$$\langle\mathcal{U}(t)\rangle = \sum_{n=0}^{\infty} P_n(t)\int_0^t dt_n\ldots\int_0^{t_2} dt_1 W_n t_1,\ldots t_n;t)\sum_{ab} p_a\int p(v_o)dv_o dv_1(av_o\,|\,\mathcal{U}(t)|\,bv_1), \tag{21}$$

where p_a is the probability for the occurrence of the state a, $p(v_o)$ is the probability that the initial velocity is v_0, $P_n(t)$ is the probability that exactly n collisions occur in time t, and $W_n(t_1,\ldots,t_n;t)\,dt_1\ldots dt_n$ is the probability that, given that n collisions occur in time t, they occur at t_1 in dt_1,... t_n in dt_n, respectively. Assuming the collisions to be described by a Poisson system of random uncorrelated points (for a

precise mathematical definition of a Poisson system and the associated probabilities, see Stratonovich 1963), we may write

$$P_n(t)=\frac{(\nu t)^n}{n!}\exp(-\nu t)$$

and

$$W_n=\frac{n!}{t^n}, \tag{22}$$

where $\nu^{-1}=\tau$ is the mean time between collisions.

Combining eqs (11), (21) and (22) and making use of the convolution property of Laplace transforms (similar mathematical steps are worked out in detail in Clauser and Blume 1971), we obtain

$$\langle \mathcal{U}(s)\rangle=\sum_{ab} p_a\int p(v_o)dv_0dv_1(av_0\,|\,[(s+\nu)-i\mathcal{H}_0{}^{\times}+ikV-\nu\mathcal{T}]^{-1}\,|\,bv_1). \tag{23}$$

At high temperatures, the excited and ground levels are equally populated i.e, $\rho_e\approx$ constant. Using eq. (9) and finding formally the Laplace transform in eq. (5) the line shape may be written

$$I(s)=\mathrm{Re}\ \mathrm{Tr}_e[d(\langle \mathcal{U}(s)\rangle d^{\dagger})]. \tag{24}$$

Now, in the effective spin-Hamiltonian formalism, the dipole operator for transitions between the excited and ground states can be represented by the raising and lowering operators (see for example Huber 1967). Thus

$$I(s)=\mathrm{Re}\ \mathrm{Tr}_e[S^{-}(\langle \mathcal{U}(s)\rangle S^{+})]. \tag{25}$$

Substituting the expression of $\langle \mathcal{U}(s)\rangle$ given in (23) in the above equation, we may then obtain

$$I(s)=\mathrm{Re}\sum_{ab}\int p(v_o)dv_odv_1\Big(av_o\,|\,\Big[\Big(-+\Big|\frac{1}{(s+\nu)-iH_0{}^{\times}+ikV-\nu\mathcal{T}}\Big|-+\Big)\Big]\,|\,bv_1\Big). \tag{26}$$

We now calculate the matrix elements of $\mathcal{T}_3$ which, from eq. (19), are given by

$$(m_1m_2\,|\,\mathcal{T}_3\,|\,m'_1m'_2)=(\langle m_1\,|\exp(i\mathbf{h}_i\mathbf{S})\,|\,m'_1\rangle\langle m'_2\,|\exp(-i\mathbf{h}_i\mathbf{S})\,|\,m_2\rangle)_{\mathrm{av}},$$

using properties of Liouville operators (Blume 1968). Since S is a spin $\frac{1}{2}$ operator, the above expression can be written (Messiah 1965)

$$\begin{aligned}&(m_1m_2\,|\,\mathcal{T}_3\,|\,m'_1m'_2)\\&=(\langle m_1\,|\,[\cos\tfrac{1}{2}h_i+2i\sin\tfrac{1}{2}h_i(\hat{h}_i\cdot\mathbf{S})\,|\,m'_1\rangle\langle m'_2\,|\,]\cos\tfrac{1}{2}h_i-2i\sin\tfrac{1}{2}h_i(\hat{h}_i\cdot\mathbf{S})\,|\,m_2\rangle)_{\mathrm{av}}\end{aligned} \tag{27}$$

where $\hat{h}_i=\mathbf{h}_i/|\,\mathbf{h}_i\,|$.

The averaging in eq. (27) has to be performed over the magnitude h_i and the directions (θ_i, ϕ_i) of $\mathbf{h}_i$. If we assume azimuthal symmetry about the z-axis (the quantization axis), the ϕ_i-dependent terms drop out, and the matrix $\mathfrak{T}_3$ can be constructed as

$$\mathfrak{T}_3 = \begin{pmatrix} 1-A & A & 0 & 0 \\ A & 1-A & 0 & 0 \\ 0 & 0 & 1+A-B-iC & 0 \\ 0 & 0 & 0 & 1+A-B+iC \end{pmatrix}, \tag{28}$$

where the rows and the columns are labelled by $++$, $--$, $+-$, and $-+$ respectively, and

$$A=(\sin^2\tfrac{1}{2}h_i\sin^2\theta_i)_{\mathrm{av}}, \quad B=(2\sin^2\tfrac{1}{2}h_i)_{\mathrm{av}}, \quad C=(\sin h_i\cos\theta_i)_{\mathrm{av}}. \tag{29}$$

We note that if the interactions are assumed to be isotropic

$$A=\tfrac{1}{3}, \; B=\tfrac{2}{3}(\sin^2\tfrac{1}{2}h_i)_{\mathrm{av}}, \; C=0. \tag{30}$$

This case corresponds to the rotational invariance of the relaxation matrix as considered by Ben-Reuven (1966). Here $\mathfrak{T}_3$ is real and hence its contribution towards any dynamical frequency shift vanishes. We retain the term C in the analysis since the associated frequency shift gives rise to an interesting effect of an asymmetry in the line contour (Rautian and Sobel'man 1967). A further removal of the assumption of azimuthal symmetry is not expected to lead to any new physical effect.

Using eqs (16) and (28), eq. (26) yields

$$I(s)=\mathrm{Re}\sum_{ab} p_a \int p(v_0)dv_0dv_1(av_0 \,|\, [s+\nu+i\Sigma\omega_jF_j+ikV-2\zeta\mathfrak{T}_1\mathfrak{T}_2]^{-1} \,|\, bv_1), \tag{31}$$

where we set

$$2\zeta=\nu(1+A-B+iC). \tag{32}$$

4. Comparison with Ben-Reuven's theory: No velocity modulation

The collision broadening of microwave spectra of gaseous molecules has been treated by Ben-Reuven (1966) based on the formalism of Baranger (1958 a,b,c), Kolb and Griem (1958), and Fano (1963). In this section, we compare our results with his. To do so, we have to adapt our expression (31) to the special situation considered by Ben-Reuven in which he *neglects the translatory motion of the molecules* and assumes rotational invariance of the relaxation matrix (i.e., ζ is real). In that case, eq. (31) reduces to

$$I(s)=\mathrm{Re}\sum_{ab} p_a(a \,|\, [s+\nu+i\sum_j \omega_jF_j-2\zeta\mathfrak{T}_1]^{-1} \,|\, b). \tag{33}$$

The collision operator now, in absence of velocity modulations, is a matrix in the $\{|a)\}$-space only.

While the present theory is based on a stochastic model in which ν and ζ enter as input parameters, Ben-Reuven's calculation relies on the resolvent operator techniques of many body theory (Zwanzig 1960; Fano 1963). Such a calculation takes into account the true interaction between the emitter and the perturber. The theory makes use of a transition matrix (analogous to our $\mathcal{T}$) which obeys the Lippman-Schwinger equation in the Liouville space. Although the formalism is quite different from the present one, the same basic assumption, namely the impact approximation, is at the heart of the calculations. It is therefore imperative to compare the results of the two approaches which may enable us to identify the parameters ν and ζ in terms of scattering amplitudes and cross-sections which appear in Ben-Reuven's calculation. The stochastic theory model may then afford us a better understanding of the nature of approximations and the physical meaning of the parameters involved in a detailed many body calculation.* Besides, it is quite straightforward to include in the theory the influence of velocity-changing collisions.

In the case treated by Ben-Reuven, the frequencies of transition are allowed to have two different values only. In terms of our model, this corresponds to the situation where the excited level, say, is split into a doublet (due to a partial lifting of the degeneracy) while the ground level remains unsplit. The emission spectrum then consists of two different lines with frequencies given by (cf. eq. 13)

$$\omega_1=\bar{\omega}+\triangle\omega, \quad \omega_2=\bar{\omega}-\triangle\omega. \tag{34}$$

If we assume that the occupational probability is the same for the two sublevels of the excited state (no finite temperature effects), then

$$p_a=\tfrac{1}{2}. \tag{35}$$

Further

$$(a|\mathcal{T}_1|b)=(b|\mathcal{T}_1|a)=\tfrac{1}{2},\ a\neq b. \tag{36}$$

Eqs (35) and (36), together with the probability conservation condition

$$\sum_b (a|\mathcal{T}_1|b)=1, \tag{37}$$

mean that

$$(a|\mathcal{T}_1|b)=\tfrac{1}{2}, \text{ for all } a \text{ and } b. \tag{38}$$

The two F-matrices can be constructed from eq. (15). As in Ben-Reuven's treatment the line shape in (33) can be obtained by inverting a 2×2 matrix. We have

$$I(\omega)=\frac{(\nu-2\zeta)\omega^2+\nu[(\triangle\omega)^2+\nu(\nu-2\zeta)]}{[\omega^2-(\triangle\omega)^2-(\nu-\zeta)^2+\zeta^2]^2+4\omega^2(\nu-\zeta)^2}, \tag{39}$$

*For an elaborate discussion of this assertion in a quite general context, see Kubo (1962).

where we set

$$s+i\bar{\omega}=-i\omega. \tag{40}$$

The line shape expression in (39) is identical to the one obtained by Ben-Reuven (1966) in his eq. (100) if the following identification of his symbols is made:

$$\triangle\omega=\omega_0+\delta,\ \nu-\zeta=\gamma. \tag{41}$$

As we have stated earlier, the expression (39) is arrived at by Ben-Reuven from a detailed examination of the bath (i.e., the rest of the gaseous particles other than the emitter). The parameters ζ and γ are related to the rate of inelastic transitions between the excited and the ground levels and are given by Ben-Reuven in terms of scattering amplitudes for binary collisions (compare with his eqs (90) and (93)). The stochastic model presented here, on the other hand, sidetracks an elaborate study of the bath variables and replaces the degrees of freedom of the bath by effective classical fields,* namely the h-fields appearing in (19). The final line shape is given in terms of the parameters ν and ζ to which direct physical meaning can be ascribed. Thus we can express ν, which measures the frequency of collisions, directly in terms of the thermodynamic parameters viz., the pressure and temperature of the gas, without having to resort to a study of the entire many body system, a task which is quite formidable in view of our too scarce knowledge of interatomic and intermolecular forces. The parameter ζ (eq. (32)) may be interpreted as the 'average' effectiveness of the collisions in causing inelastic transitions between the levels.

We may now discuss some special forms of the shape factor $I(\omega)$ which from eqs (33)-(38) can also be expressed as

$$I(\omega)=\mathrm{Re}\,\frac{i}{2}\left[\frac{1-i\zeta/\sqrt{(\triangle\omega)^2-\zeta^2}}{\omega+i(\nu-\zeta)+\sqrt{(\triangle\omega)^2-\zeta^2}}+\frac{1+i\zeta/\sqrt{(\triangle\omega)^2-\zeta^2}}{\omega+i(\nu-\zeta)-\sqrt{(\triangle\omega)^2-\zeta^2}}\right]. \tag{42}$$

4.1. If ζ is zero (*no inelastic transitions*), we get

$$I(\omega)=\mathrm{Re}\,\frac{i}{2}\left[\frac{1}{\omega+\triangle\omega+i\nu}+\frac{1}{\omega-\triangle\omega+i\nu}\right]. \tag{43}$$

Each collision now has an effect of changing the splitting between the levels only without causing a direct transition between them. As expected, eq. (43) is the familiar Van Vleck-Weisskopf line shape (Ben-Reuven 1969).

4.2. If the effective field **h** the emitter experiences during a collision is zero, $\mathfrak{I}_3$ becomes a unit matrix (see eq. (28)). This corresponds to the case where there is frequency modulation only and no phase modulation. We now have from eqs (29) and (32),

$$\zeta=\tfrac{1}{2}\nu, \tag{44}$$

and

$$I(\omega)=\mathrm{Re}[-i\omega+i(\triangle\omega)^2/(\omega+i\nu)]^{-1}. \tag{45}$$

*Compare with the classical path approximation of Baranger (1962).

When $\nu \ll \triangle\omega$, eq. (45) yields two sharp lines centred around $\omega = \pm\triangle\omega$. On the other hand, when $\nu \gg \triangle\omega$, the spectrum collapses into a single 'motionally narrowed' line (Abragam 1961).

4.3. When either ν is small (buffer gas at low density) or $(1+A-B)$ is small (weak inelastic transitions), the parameter ζ (eq. (32)) is finite but smaller than $\triangle\omega$. In that case, the radical in (42) is real and contributes to the shift. One now obtains a superposition of two lines centred around $\pm\sqrt{[(\triangle\omega)^2-\zeta^2]}$, each broadened slightly by an amount $(\nu-\zeta)$.

4.4 When ζ is larger than $\triangle\omega$ (buffer gas at higher density), the radical in (42) is imaginary and contributes to the width. This phenomenon is generally called the pressure broadening of spectral lines.

4.5. Finally, when $\zeta \gg \triangle\omega$, $I(\omega)$ reduces to the familiar Debye shape

$$I(\omega) = \mathrm{Re}\,\frac{i}{\omega + i(\nu - 2\zeta)} = \mathrm{Re}\,\frac{i}{\omega + 2i\nu A}, \tag{46}$$

using eqs (32) and (30). This yields the so called non resonant spectra (Ben-Reuven 1966).

We conclude this section by remarking that the results given here can be generalized, by making certain special assumptions about the transition matrix $\mathfrak{I}_1$, to cases where the frequencies of transition can assume more than just two different values (Dattagupta and Blume 1974a).

5. Effect of velocity-changing collisions in the strong collision model

As we mention in section 1, the existing treatments of collisional effects on spectral lines in gases deal at a time with one (or at best two) of the three distinct effects of a collision, namely, the frequency, the phase and the velocity modulations. Thus almost all the many body calculations (see, for example, Ben-Reuven 1966) involve only the frequency and the phase modulations which are caused by the interaction between the emitter and the perturbers. The velocity distribution of the emitter is usually assumed to be Maxwellian and the resultant Doppler broadening of the lines is added (convoluted) to the broadening caused by the interaction. There are in the literature some attempts to calculate the simultaneous effects of velocity-changing collisions and interactions on the line shape (Galatry 1961, Rautian and Sobel'man 1967). Of these, Galatry considers only the case where *not all* collisions lead to changes in the velocity of the emitter and those which do, have no associated effect due to the interaction. Rautian and Sobel'man, on the other hand, do study the situation where the same collision is responsible for the simultaneous effects. However, these authors neglect the frequency modulation and treat the phase modulation in a purely classical way. Ben-Reuven (1975) has recently extended the use of Liouville-space methods to include velocity effects. The stochastic theory model presented here lends a different approach to the problem wherein one can deal with all the three effects of a collision in a unified way with the aid of one basic assumption, namely the impact

approximation. In addition, it describes in a simple manner the quantum mechanical origin of the phase modulation.

The physical picture we adopt for the velocity modulation effect is essentially similar to that of Rautian and Sobel'man (1967). But unlike these authors who employ a Boltzmann like kinetic equation for a distribution function of the velocities, we use a velocity matrix whose eigenvalues are the possible velocities of the emitter and a collision operator which induces transitions from one velocity to another (section 3).

To demonstrate the interplay between the frequency, phase, and velocity modulation effects of a collision, we treat a special form of the collision operator $\mathcal{T}_2$ which is amenable to a considerable amount of analytic study. This is the so called strong collision model which, although is valid strictly when the perturber is much heavier than the emitter, has nevertheless, a wider applicability than the weak collision or the diffusion model (Rautian and Sobel'man 1967). In the strong-collision model, each collision is assumed to render the velocity of the emitter completely random with no memory of the initial velocity before the collision. This fact can be mathematically expressed as

$$(v_i \mid \mathcal{T}_2 \mid (v_f) = f(v_f), \tag{47}$$

a function of the final velocity alone.

The transition matrix $\mathcal{T}_2$ is required to satisfy the detailed balance condition (see for example Dattagupta and Blume 1974a).

$$p(v_i)\,(v_1 \mid \mathcal{T}_2 \mid v_f) = p(v_f)\,(v_f \mid \mathcal{T}_2 \mid v_i), \tag{48}$$

where $p(v)$ is the equilibrium occupational probability or the Boltzmann factor corresponding to the velocity v of the emitter. For sufficiently dilute gases in which the only important collisions are binary, $p(v)$ may be assumed to be Maxwellian:

$$p(v) = \sqrt{\frac{1}{2\pi\bar{v}^2}}\,\exp(-v^2/2\bar{v}^2), \tag{49}$$

where the mean-square velocity is defined by

$$\bar{v}^2 = \int_{-\infty}^{\infty} v^2 p(v)\,dv \tag{50}$$

A comparison of eqs (47) and (48) allows us to write

$$f(v) = \alpha p(v), \tag{51}$$

where α is a dimensionless constant. Further, the probability conservation conditions

$$\int_{-\infty}^{\infty} (v_i \mid \mathcal{T}_2 \mid v_f)\,dv_f = 1, \quad \int_{-\infty}^{\infty} p(v_f)\,dv_f = 1, \tag{52}$$

fix

$$\alpha = 1, \tag{53}$$

so that eq. (47) yields

$$(v_i \mid \mathcal{T}_2 \mid v_f)=p(v_f). \tag{54}$$

Returning now to the case studied in section 4 in which only two possible values of frequency are allowed, the line shape from eq. (31) may be written

$$I(s)=\mathrm{Re}\sum_{ab} p_a \int p(v_0)dv_0dv_1(av_0 \mid G(s) \mid bv_1), \tag{55}$$

where $p_a=\frac{1}{2}$ and

$$G(s)=[s+\nu+i\sum_{j=1}^{2}\omega_j F_j+ikV-2\zeta\ \mathcal{T}_1\ \mathcal{T}_2]^{-1}. \tag{56}$$

We have

$$G(s)=G^0(s+\nu)+2\zeta\ G^0(s+\nu)\ \mathcal{T}_1\ \mathcal{T}_2\ G(s), \tag{57}$$

where

$$G^0(s+\nu)=[s+\nu+i\sum_{j=1}^{2}\omega_j F_j+ikV]^{-1}. \tag{58}$$

Denoting

$$\langle G(s)\rangle=\tfrac{1}{2}\sum_{ab}\int p(v_0)dv_0dv_1(av_0 \mid G(s) \mid bv_1), \tag{59}$$

and making use of the closure property,

$$\sum_a \mid a)(a \mid =1,$$

and

$$\int dv \mid v)(v \mid =1, \tag{60}$$

we obtain

$$\langle G(s)\rangle=\langle G^0(s+\nu)\rangle+2\zeta\ \tfrac{1}{2}\sum_{abcd}\int p(v_0)dv_0dv_1\ dv_2\ dv_3$$

$$\times(av_0 \mid G^0(s+\nu) \mid cv_2)\ (c \mid \mathcal{T}_1 \mid d)\ (v_2 \mid \mathcal{T}_2 \mid v_3)(dv_3 \mid G(s) \mid bv_1), \tag{61}$$

where

$$\langle G^0(s+\nu)\rangle=\tfrac{1}{2}\sum_{ab}\int p(v_0)dv_0dv_1(av_0 \mid G^0(s+\nu) \mid bv_1). \tag{62}$$

Using eqs (38) and (54) in (61) we get

$$\langle G(s)\rangle = \langle G^0(s+\nu)\rangle + 2\zeta \langle G^0(s+\nu)\rangle \langle G(s)\rangle. \tag{63}$$

Combining eqs (55), (59) and (63), the line shape can finally be written

$$I(s)=\mathrm{Re}\ \frac{1}{\langle G^0(s+\nu)\rangle^{-1}-2\zeta}, \tag{64}$$

where, from eqs (58), (62), (15) and (17),

$$\langle G^0(s+\nu)\rangle = \frac{1}{2}\sum_{j=1}^{2} \int d\nu \frac{p(\nu)}{s+\nu+i\omega_j+ik\nu}. \tag{65}$$

To gain insight into the final result several special cases may now be discussed.

5.1. *No frequency modulation*

In this case $\triangle\omega=0$, and $\omega_j=\bar{\omega}$, from eq. (13). Equations (64) and (65) then yield

$$I(\omega)=\mathrm{Re}\ \frac{\int d\nu \dfrac{p(\nu)}{\nu-i(\omega-k\nu)}}{1-2\zeta\int d\nu \dfrac{p(\nu)}{\nu-i(\omega-k\nu)}}, \tag{66}$$

using (40). This expression is identical to eq. (7.6) of Rautian and Sobel'man (1967). As stated earlier, eq. (66) is derived by these authors by solving the Boltzmann kinetic equation for the velocity distribution function. The kernal that appears in the collision integral of the Boltzmann equation assumes a simple form in the strong collision model and enables one to write the spectral line shape in a closed form such as eq. (66). The phase modulation factor 2ζ whose quantum mechanical origin is discussed in section 3, is treated by Rautian and Sobel'man (1967) in a completely classical way. If we compare eq. (7.4) of the latter authors with our eq. (32), we can make the identification

$$\Gamma = \nu(B-A),\ \triangle = \nu C. \tag{67}$$

Eq. (66) and its possible experimental verification are discussed by Rautian and Sobel'man. In particular, these authors point out the significance of the imaginary part of ζ (viz., the term νC) in being responsible for an asymmetry in the line contour. The latter feature marks clearly the distinction between the case where the phase and the velocity modulations occur in different collisions (Galatry 1961) and the one where they occur in the same collisions.

5.2. *Very slow collisions*

This situation pertains to a buffer gas with a very low density so that $\nu \approx 0$ i.e., the mean free time between collisions is infinitely large. Eqs (64) and (65) then reduce to

$$I(s) \approx \mathrm{Re}\,\frac{1}{2}\sum_{j=1}^{2}\int dv\,\frac{p(v)}{s+i\omega_j+ikv}$$

$$= \mathrm{Re}\,\tfrac{1}{2}\sum_{j=1}^{2}\int_0^\infty dt\,\exp(-st-i\omega_j t)\int_{-\infty}^{\infty} dv\,\exp(-ikvt)p(v). \quad (68)$$

From eq. (49),

$$\int_{-\infty}^{\infty} dv\,p(v)\exp(-ikvt) = \exp(-\tfrac{1}{2}k^2\overline{v^2}t^2). \quad (69)$$

Substituting eqs (40) and (69) in (68) and performing the t-integration, we obtain

$$I(\omega) = \sqrt{\frac{\pi}{8k^2\overline{v^2}}}\left[\exp-\left(\frac{\omega-\triangle\omega}{2k^2\overline{v^2}}\right)+\exp-\left(\frac{(\omega+\triangle\omega)^2}{2k^2\overline{v^2}}\right)\right]. \quad (70)$$

The spectrum now consists of two distinct lines centered around $\pm\,\triangle\omega$, each Doppler broadened by an amount $(8k^2\overline{v^2}\ln 2)^{\frac{1}{2}}$. The two lines correspond to the emitters found in one or the other of the two sub-levels associated with the excited state. Since collision-induced transitions between the sub-levels is extremely slow in this case, the observed spectrum is an incoherent superposition of the two lines (no interference).

5.3. *Fast collisions*

To investigate this case, it is useful to write eq. (65) with the aid of eq. (69) as

$$\langle G^0(s+\nu)\rangle = \tfrac{1}{2}\sum_{j=1}^{2}\int_0^\infty dt\,\exp\left[-(s+i\omega_j+\nu)t-\tfrac{1}{2}k^2\overline{v^2}t^2\right]$$

$$= \sqrt{\frac{\pi}{8k^2\overline{v^2}}}\sum_{j=1}^{2}\exp(q_j^2/2k^2\overline{v^2})\,\mathrm{erfc}\sqrt{\frac{q_j^2}{2k^2\overline{v^2}}}, \quad (71)$$

where we put

$$q_j = (s+i\omega_j+\nu), \quad (72)$$

and express the Laplace transform of a Gaussian in terms of the complimentary error function (Abramowitz and Stegun 1965) defined by

$$\text{erfc } Z = \frac{2}{\sqrt{\pi}} \int_{Z}^{\infty} \exp(-Z'^2)\, dZ'. \tag{73}$$

When the rate of collisions is high as in a dense buffer gas, $\nu > (k^2\overline{\nu^2})^{\frac{1}{2}}$, we may make use of the asymptotic expansion (Abramowitz and Stegun 1965)

$$e^Z \text{erfc } \sqrt{Z} \sim \frac{1}{\sqrt{\pi Z}}\left[1 + \sum_{m=1}^{\infty} (-1)^m \frac{1.3 \ldots (2m-1)}{(2Z)^m}\right], \tag{74}$$

to write eq. (71) as

$$\langle G^0(s+\nu)\rangle \sim \frac{1}{2}\sum_{j=1}^{2} \frac{1}{q_j}\left[1 + \sum_{m=1}^{\infty} (-1)^m \frac{1.3 \ldots (2m-1)}{(q_j^2/k^2\overline{\nu^2})^m}\right]. \tag{75}$$

The line shape is now given by eqs (64) and (75).

As a further specialization, if we now consider the case looked at by Rautian and Sobel'man (1967) of no frequency modulation, we have $\Delta\omega = 0$, and from eqs (72) and (40).

$$q_j = \nu - i\omega, \tag{76}$$

independent of j. Equation (75) then yields

$$\langle G_0(s+\nu)\rangle^{-1} \approx \nu - i\omega + \frac{k^2\overline{\nu^2}}{\nu - i\omega} - \frac{3(k^2\overline{\nu^2})^2}{(\nu - i\omega)^3} + \ldots \tag{77}$$

In that case, the line shape, from eq. (64) can be expressed as

$$I(\omega) = \text{Re}\left[\Gamma - i(\omega - \Delta) + \frac{k^2\overline{\nu^2}}{\nu - i\omega} - \frac{3(k^2\overline{\nu^2})^2}{(\nu - i\omega)^3} + \ldots\right]^{-1}, \tag{78}$$

where we have used eqs (77), (32) and (67). It is clear from the above equation how the velocity modulation affects the width and the location of the spectral line.

We find in the above that at least in the strong collision model, the simultaneous effects of the frequency, phase and velocity modulations due to a collision, can be examined in rather satisfactory analytic detail. In contrast, the mathematical application of the general result (31) in the case of the weak collision model where the collision operator obeys a diffusion equation of the Fokker-Planck type (Rautian and Sobel'man 1967) was found to be much more complicated and we were unable to arrive at an analytic expression for the line shape.

6. Conclusions

We examine in this paper the effect of collisions on the atomic or the molecular spectra in gases. The particular case of the emitter imbedded in a foreign buffer gas is treated. It is argued that a collision can simultaneously give rise to three distinct effects namely the frequency, the phase, and the velocity modulations. We treat all these effects in a stochastic model in which the buffer gas is regarded as a heat bath in thermal equilibrium which, through collisions with the emitter, makes the velocity and the Hamiltonian of the latter, randomly time dependent. As in the familiar impact approximation the collisions are also assumed to be governed by a random Poisson distribution. The entire dynamics of the problem is described basically in terms of one parameter, namely the mean free time of collisions. We show that the frequency modulation is important when the rate of collisions is comparable to the frequency values. Therefore, even for a dilute gas, in which the rate of collisions is not too high such studies may be useful in microwave and far-infrared spectroscopy and some other cases as well. While treating the frequency modulation effect, only two frequency values are considered for mathematical simplicity. The calculations can however be generalized in some cases when more than just two frequencies are involved. In section 4, we display a detailed comparison between our stochastic theory results and those obtained by Ben-Reuven from an *ab-initio* treatment. Such a comparison, in our opinion, is quite important for it allows one to obtain a physical understanding of the approximations used in a many body calculation. The effect of velocity modulation is introduced in sect. 5 in terms of the strong collision model which yields the line shape in a closed analytic form. Again the results of Rautian and Sobel'man who study only the phase and velocity modulation effects are obtained as special cases of the present theory.

Although we discuss here the emission (or the absorption) problem only, the ideas developed in this paper are expected to be of importance in the scattering case also, such as the Raman spectra (Fiutak and Van Kranendonk 1962) or the resonant scattering in gases (Huber 1969, Omont *et al* 1972). The mathematical formalism in the scattering case is much more complicated but it is expected that some progress can still be made in at least those cases in which the impact approximation is valid. Using assumptions similar to the impact approximation Afanas'ev and Gorobchenko (1974) have recently investigated the resonant scattering of nuclear gamma rays in solids. These authors are obviously interested in the frequency modulation effect only caused by fluctuations in the extra nuclear solid state environment. It may now be useful to extend the calculations presented here for the emission lines to the case of scattering of light by gaseous atoms or molecules in order to examine the simultaneous effects of the frequency, phase and velocity modulations on the differential scattering crossection.

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