THE THEORY OF INTERCOLLISIONAL INTERFERENCE EFFECTS IN ARBITRARY GAS MIXTURES

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A KINETIC THEORY OF INTERCOLLISIONAL INTERFERENCE EFFECTS IN ARBITRARY GAS MIXTURES

by

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of the requirements for the degree of
Master of Science

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ABSTRACT

A kinetic theory of intercollisional interference effects in collision-induced translational absorption by arbitrary binary gas mixtures has been developed. Expressions have been derived for the intercollisional dip in which no assumptions about the relative concentration ratios or relative masses of the two constituents have been made. The variation of the halfwidth of the dip with the concentration ratio of the mixture has been obtained. The halfwidths at the infinitely dilute endpoints, $n_A/n_B \to 0$ and $n_A/n_B \to \infty$, predicted by this theory are in agreement with previous theoretical results. This theory also shows reasonably good agreement with the experimental data on the line shape as a function of $n_A n_B$ for various concentration ratios. Our curves provide the correct qualitative behaviour of the line shape.

In addition, expressions have been developed for intercollisional interference effects in collision-induced translational absorption by mixtures of arbitrary composition. That is, the above theory has been extended to include mixtures in which the number of constituents is arbitrary.

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LIST OF SYMBOLS

Symbols which occur only in a few successive pages are not in general included in this list.

When a parameter is closely related to several other variables in an obvious way, we only include one as an example with the page on which it is defined. The other definitions are usually found on the same page or adjacent pages.

Special symbols not included in the list for Chapters 1, 2, and 3 are included on page xv.

CHAPTER 1

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
A	molecular species A	7
A_1	molecule of species A	7
$\tilde{A}(\nu)$	absorption coefficient	3
$C(\tau)$	autocorrelation function	12
D	diffusion coefficient of molecule A_1	9
$\vec{f}(R)$	intermolecular force	9
$\vec{f}(t)$	force on molecule A_1 at time t	7
$\vec{f}^{(ab)}_{AB}(t)$	intermolecular force between molecule a of species A and molecule b of species B at time t	9
J	rotational angular momentum quantum number	5
m	mass of molecule A_1	8
$\vec{M}(t)$	total induced dipole moment at time t	10

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
m_A	mass of molecule a of species A	9
N_A	number of molecules of species A	9
T	temperature	2
v	vibrational quantum number	5
$\vec{v}(t)$	velocity of molecule A_1 at time t	7
$\dot{\vec{v}}_{Aa}(t)$	acceleration of molecule a of species A at time t	10
$V_A^{(ij)}(\omega)$	$\int_{-\infty}^{\infty} e^{i\omega\tau} \langle \vec{v}_{Ai}(t) \cdot \vec{v}_{Aj}(t+\tau) \rangle dt$	12
$w(\omega)$	(reduced) line shape [power spectrum of total induced dipole moment, spectral density]	14
$W_f(\omega)$	spectral density of the force	8
$W_v(\omega)$	spectral density of the velocity	8
$\tilde{\alpha}_1$	binary absorption coefficient	3
$\tilde{\alpha}_2$	ternary absorption coefficient	3
$\vec{\mu}(R)$	induced dipole moment	9
$\vec{\mu}_{AB}^{(ab)}(t)$	dipole moment induced in molecule a of species A and molecule b of species B at time t	9
ρ_a	dilute gas number density	3
ρ_p	perturbing gas number density	3
τ_c	characteristic time between collisions	5
τ_d	duration of collision	1
ω	circular frequency	8

CHAPTER 2 AND CHAPTER 3

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
A	molecular species A	2
a	molecule a of species A	22
a_i	temporal superposition coefficient, 0 for AA,BB collisions, 1 for AB;BA collisions.	27
$\mathcal{A}_A(c_1)$	$\int_0^\infty dc'_1 \mathcal{A}_A(c'_1 \| c_1)$ for AB collisions	39
$\mathcal{A}_A(c'_1 \| c_1)$	$<\overline{\vec{\mu}}(g,\vec{C}) \cdot \hat{c}_1>_{\xi,\phi,g,\phi_g}$ for AB collisions.	39
$\mathcal{B}_A(c'_1 \| c_1)$	$<\overline{\vec{\mu}}(g,\vec{C}) \cdot \hat{c}'_1>_{\xi,\phi,g,\phi_g}$ for AB collisions.	41
$C(\tau)$	autocorrelation function of the total induced dipole moment	22
$\vec{C}$	$\vec{c}\,'_1-\vec{c}_1$, apse line (see figure 2.2)	35
C	intracollisional part of spectrum	61
$C(\tau)_{intra}$	intracollisional autocorrelation function	29
$C(\tau)_{inter}$	intercollisional autocorrelation function	29
$C_n^A(\tau)$	n^{th} correlation coefficient, due to collision sequences of molecules of species A	30
$C^A_{i,i+n}$	correlation coefficient	30
$\vec{c}\,'_1$	velocity of molecule 1 before the collision (see figure 2.2)	34

SYMBOLS	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
c_1'	(c_1', ξ, ϕ) : spherical polar coordinates of the velocity of molecule 1 after a collision (see figure 2.2)	34
g	$\lvert \vec{c}_2 - \vec{c}_1 \rvert = \lvert g_{12} \rvert$, magnitude of g_{12}	34
$G_A(\omega, c_1)$	solution to the Fredholm equation $A_A(c_1) = \int_0^\infty dc_1' \Delta_A(c_1' \mid c_1) G_A(\omega, c_1')$	48
i	collision label (represents the collision variables of the i^{th} collision, appears as subscript)	25
k	Boltzmann's constant	26
$K_A(c_1' \mid c_1)$	$\int_0^\pi d\xi \, \sin\xi \int_0^\infty dg \bar{\mu}^2 P_{AB}(g, \xi, c_1' \mid c_1)$	50
$\vec{M}(t)$	total induced dipole moment	22
m_A	mass of molecule a of species A	22
m_0	$m_A + m_B$	26
n	1. denotes the n^{th} subsequent collision from an arbitrarily chosen initial collision i (always occurs as subscript)	29
	2. $n_A + n_B$, number density of mixture	78
n_A	number density of molecular species A	22
N_{AB}	three dimensional collision frequency	25
$p(x_i)$	distribution of collision intervals, x_i	31
$P(g, \xi, c_1' \mid c_1)$	conditional probability distribution of g, ξ, and c_1 for a given c_1	36

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
$P(c_i)$	Maxwell-Boltzmann distribution of speeds	36
$p_{AB}(x_i)$	distribution of collision intervals, x_i, for AB collisions	32
$\tilde{p}_{AB}(\omega)$	$\int_o^\infty p_{AB}(x_i)e^{-i\omega x_i}dx_i$	33
S_{AB}	$2\Sigma_{AB}\sqrt{2kTm_o/\pi m_A m_B}$	26
T	1. temperature 2. time (always used in limiting expressions)	25 30
t_i	time of i^{th} collision	27
u_{AB}	relative frequency of AB collisions in the collision history of a molecule of species A	27
V	volume of system	25
$W(\omega)$	(reduced) line shape function, power spectrum	22
$w(\omega)$	$W(\omega)/N_{AB} \cdot V$	51
$W(\omega)_{inter}$	intercollisional line shape function	31
$W(\omega)_{intra}$	intracollisional line shape function	50
$W_n^A(\omega)$	n^{th} contribution to $W(\omega)_{inter}$ due to collision sequences of molecules of species A	31
x_A	mole fraction of species A	69

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
x_i	$t_{i+1}-t_i>0$, time interval between collisions	30
α_A	intercollisional part of spectrum	61
γ_A	measure of depth of intercollisional dip	63
$\Delta_{AB}(c_1'\|c_1)$	$<\hat{c}_1 \cdot \hat{c}_1'>_{\xi,\phi,g,\phi_g}$ for AB collisions	40
$\Delta_A(c_1'\|c_1)$	$\tilde{p}_{AB}(\omega)u_{AB}\Delta_{AB}(c_1'\|c_1)+\tilde{p}_{AA}(\omega)u_{AA}\Delta_{AA}(c_1'\|c_1)$	47
$\tilde{\Delta}_A$	average value of $\Delta_A(c_1'\|c_1)$	58
$\tilde{\Delta}_{AB}$	average value of $\tilde{\Delta}_{AB}\overline{(c_1'\|c_1)}$, chosen to be the mean persistance-of-velocity	59-60
η	angle between $\vec{c}_1$ and $\vec{C}$ (see figure 2.2)	37
$\vec{\mu}^{(ab)}(t)$	dipole moment induced in molecule a of species A by molecule b of species B, at time t.	22
$\vec{\mu}^{(a)}(t)$	total dipole moment induced by molecule a of species A in all other molecules, at time t	24
$\vec{\mu}_i(t)$	dipole moment induced in the i^{th} collision	25
$\vec{\mu}_i(\omega)$	Fourier transform of $\vec{\mu}_i(t)$	33
$\overline{\vec{\mu}}_i$	$\int_{-\infty}^{\infty}\vec{\mu}_i(\tau)d\tau=\vec{\mu}_i(0)$, time average of $\vec{\mu}_i(\tau)$ equivalent to value of $\vec{\mu}_i(\omega)$ at zero frequency	34
ν_A	collision frequency of a single molecule of species A with both A and B molecules	26

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
ν_{AB}	average collisional frequency of AB collisions of a single molecule of species A	65,67
ξ	(c_1', ξ, ϕ): spherical polar coordinates of the velocity of molecule 1 after a collision (see figure 2.2)	34
σ	rigid-sphere diameter	66,68
$\sum_{AB}$	total scattering cross section for AB collisions	26
τ	arbitrary time interval	22
τ_c	characteristic time between collisions	22
τ_d	duration of collision	22
ϕ	(c_1', ξ, ϕ): spherical polar coordinates of the velocity of molecule 1 after collision (see figure 2.2)	34
ϕ_g	azimuth of $\vec{g}_{12}$	34
ω	circular frequency	22
$\omega_{\frac{1}{2}}$	halfwidth of the intercollisional spectrum	71

ADDITIONAL NOTATION IN CHAPTER 3

a_α	molecule of species α	86
$A_\varepsilon^\gamma(c_1)$	$\int_0^\infty dc_1 A_\varepsilon^\gamma(c_1' \mid c_1)$ $A_\varepsilon^\gamma(c_1' \mid c_1) = \langle \vec{\bar{\mu}}(g, \vec{C}) \cdot \hat{c}_1 \rangle_{\xi, \phi, g, \phi_g}$ for $\varepsilon\gamma$ collisions	98

SYMBOL	DESCRIPTION AND/OR DEFINITION AS APPLICABLE	REFERENCE PAGE
$B_{\varepsilon}^{\delta}(c_1' \mid c_1)$	$\langle \vec{\bar{\mu}}(g,\vec{C}) \cdot \hat{c}_1' \rangle_{\xi,\phi,g,\phi_g}$ for $\varepsilon\delta$ collisions	98
$G_{\varepsilon}^{\gamma}(\omega,c_1)$	solution to the Fredholm equation, $A_{\varepsilon}^{\gamma}(c_1)+\int_0^{\infty} dc_1' \Delta_{\varepsilon}(c_1' \mid c_1) G_{\varepsilon}^{\gamma}(\omega,c_1')$	102
N_{α}	number of molecules of species α	86
$\alpha,\beta,\ldots,\omega$	molecular species $\alpha,\beta,\ldots,\omega$	86
$\Delta_{\varepsilon\chi}(c_1' \mid c_1)$	$\langle \hat{c}_1 \cdot \hat{c}_1' \rangle_{\xi,\phi,g,\phi_g}$ for $\varepsilon\chi$ collisions	100
$\Delta_{\varepsilon}(c_1' \mid c_1)$	$\sum_{\chi} \tilde{p}_{\varepsilon\chi}(\omega)\, u_{\varepsilon\chi} \Delta_{\varepsilon\chi}(c_1' \mid c_1)$	100

TIME AND COLLISIONAL AVERAGING NOTATION

$\langle \ldots \rangle$	time average; Chapters 1, 2, and 3	8
$\langle \ldots \rangle_i$	collisional average; Chapter 2	25
$\langle \ldots \rangle_i^{\varepsilon\varepsilon'}$	collisional average over $\varepsilon\varepsilon'$ collisions; Chapter 3	90
$\langle \ldots \rangle^{\varepsilon}$	time average over ε collisions; Chapter 3	93,94

CHAPTER 1

INTRODUCTION

1.1 Collision Induced Absorption

The phenomenon whereby molecular collisions give rise to optical transitions forbidden in free molecules, is referred to as collision-induced absorption. When molecules collide, the intermolecular interaction causes a distortion of the charge configuration of the colliding molecules. At low densities, one can neglect ternary and higher order collisions and only consider the effects due to binary encounters. Such an encounter between unlike non-polar molecules induces a dipole moment that lasts for the duration of the collision, τ_d. Thus, light can be emitted or absorbed by the colliding pair, via this temporary dipole moment. For polyatomic molecules, this induced dipole moment is modulated by the rotational, vibrational and relative translational motions of the two molecules. Thus, absorption of light due to this dipole moment gives rise to rotation, rotation-vibration, and pure translational spectra. The rotation and vibration spectra are centred about the rotational and vibrational frequencies of the colliding molecules. Collisions between monatomic molecules will give rise to a pure translational spectrum in the far infrared extending down to zero frequency.

A characteristic property of collision-induced absorption spectra is that the integrated intensities are approximately proportional to the square of the density of the gas, or in the case of a binary gas mixture, approximately proportional to the product to the partial densities. Another important characteristic is due to the fact that absorption can only take place for the duration of a collision, τ_d, which is typically of the order of 10^{-13} s. The resulting spectra then have widths of the order of τ_d^{-1}, roughly 100 cm^{-1}, hence are very broad. Because of this dependence on τ_d, the line shape has a marked temperature dependence with $\omega_{\frac{1}{2}}$ proportional to $T^{-\frac{1}{2}}$.

The phenomenon of collision-induced absorption was first discovered by Crawford, Locke, and Welsh (1949), when they observed collision-induced vibrational spectra in compressed and liquid oxygen. Subsequently collision-induced spectra in pure hydrogen, hydrogen-rare gas, and rare gas mixtures have been studied extensively. Much of the experimental work on collision-induced absorption was carried out by H. L. Welsh and collaborators at Toronto. Detailed descriptions of their research have been given by Welsh (1972) and Welsh (1974). Many of the theoretical contributions to the study of integrated collision-induced spectra were due to Van Kranendonk et al (Van Kranendonk and Bird 1951; Van Kranendonk 1957, 1958, 1959; Van Kranendonk and Kiss 1959; Poll and Van Kranendonk 1961). Also, spectral line shape calculations have been carried out by Tanimoto (1965), Levine and Birnbaum (1967), Levine (1967), Okada, Kajikawa and Yamamoto (1968), Sears (1968), Lewis and Van Kranendonk (1972) and Lewis (1972). A bibliography on publications in collision-induced absorption appearing before 1975 has been compiled by Rich and McKellar (1976).

1.2 Many-Body Effects in Collision-Induced Absorption

The collision-induced absorption spectrum of a gas is modified by several many-body effects as the density of the gas is increased. For a binary gas mixture, the integrated absorption coefficient is given to a high degree of accuracy by

$$\int_0^\infty \tilde{A}(\nu)d\nu = \tilde{\alpha}_1\rho_a\rho_p + \tilde{\alpha}_2 O(\rho^3) \qquad (1.1)$$

where ρ_a and ρ_p are the densities of the dilute gas and the perturbing gas respectively, and $\tilde{\alpha}_1$ and $\tilde{\alpha}_2$ are the binary and ternary absorption coefficients (Van Kranendonk 1957). In this work we assume we will be dealing with densities low enough so that the righthand side of (1.1) can be approximated by the first term only. This is equivalent to assuming that the absorption is entirely due to binary collisions, and neglects the many-body effect of ternary and higher order collisions. At liquid densities in dilute H_2-foreign gas mixtures, it appears that the H_2 molecule can be temporarily trapped by a cage of foreign gas atoms which lends a diffusive character to the motion of this molecule. Hence, the effective duration of a collision with a given foreign gas atom is increased, and thus the line shape is narrowed (Zaidi and Van Kranendonk 1971). This is observed in the characteristic line narrowing of the rotational lines in the induced vibrational spectrum of H_2-Ar mixtures (de Remigis, Mactaggart, and Welsh 1971). This same mechanism of temporary trapping by foreign gas atoms, when it involves two or more H_2 molecules is believed to give rise to the appearance of H_2 double transitions in the first overtone region of H_2 in dense H_2-Ar mixtures (Mactaggart 1971). The above mentioned phenomena of pressure narrowing and H_2 double transitions only become significant at near liquid densities and will not be treated here. However, even at relatively low densities, many-body effects have important consequences in collision-induced absorption spectra. The correlations that exist between successive binary collisions experienced by a molecule give rise to the phenomenon of intercollisional interference. Intercollisional interference is the subject of this thesis and is described in detail below.

1.3 Intercollisional Interference in Collision-Induced Absorption

The force pulses on a molecule in a gas in successive collisions are negatively correlated, i.e., they tend to point in opposite directions. If no such correlation were present, the molecule would perform an unrestricted random walk in velocity space, and hence the expectation value of its energy would increase without limit in time (Chandrasekhar 1943). The negative correlation is strong enough so that the spectral density of the total force, on a particular molecule in the gas, dips to zero at zero frequency. The behavior of the spectral density at zero frequency will be discussed in more detail in section 1.4. This force correlation has important effects in nuclear electric dipole relaxation, as pointed out by Purcell (1960). He obtained an expression for the spectral density of the force which showed that the width of the dip is characterized by the mean collisional frequency, τ_c^{-1}. Thus, the width of the dip is proportional to the density.

This force correlation also has important consequences in collision-induced spectra, as shown by Van Kranendonk (1968). The isotropic part of the induced dipole moment is due to the short range overlap of the molecular charge clouds, and is directed parallel or nearly parallel to the intermolecular force. As a result of the negative correlation in the force pulses, there arises a negative correlation in the isotropic part of the dipole moments induced in successive collisions. This leads to destructive interference in the radiation processes due to this isotropic component, occurring during successive binary collisions. Hence, in H_2-foreign gas mixtures dilute in H_2, the collision-induced fundamental vibrational band of hydrogen, the Q branch ($\Delta v = 1$, $\Delta J = 0$), has an intercollisional interference dip, the halfwidth of which is approximately linear in the density of the foreign gas. The two components formed by this dip, denoted Q_P and Q_R, are related by a Boltzmann factor (Hunt and Welsh 1964).

The anisotropic part of the dipole moment, on the other hand, is induced primarily by the longer ranged quadrupolar interaction (Van Kranendonk and Bird 1952; Van Kranendonk 1957, 1958). It is highly dependent on the orientation of the colliding molecules, and not in general directed parallel to the intermolecular force. As a result, the negative correlation that is present in the isotropic component of the dipole moments induced in successive collisions will be much weaker for the anisotropic component of these induced dipole moments. Thus, the lines that are due to this anisotropic component, the S lines ($\Delta J = 2$), will only weakly show the dip that is the experimental manifestation of intercollisional interference (Poll, Hunt and Mactaggart 1975; experimental work by Reddy and Lee (1968) and Reddy and Chang (1973)).

It is evident that pure translational spectra should also show an intercollisional interference dip in the spectral density of the total induced dipole moment. This was predicted by Van Kranendonk (1968), who showed that in rare gas mixtures a dip should occur about zero frequency, with a width equal to τ_c^{-1}. This was verified by Marteau, Vu and Vodar (1968), who observed a number of absorption spectra in various compressed rare gas mixtures down to a minimum frequency of 16 cm^{-1}. Spectra of gas mixtures at a minimum frequency of about 1 cm^{-1} later obtained by Muc, Reeser and Dagg (1971), and Dagg, Reesor and Urbaniak (1974), also confirmed this result.

In pure hydrogen, intercollisional interference is manifested in a dip occurring in the Q branch of the fundamental vibrational band, the halfwidth of which is approximately linear in the density of hydrogen. The first overtone region, which consists of the pure overtone and double vibrational transitions, is due entirely to quadrupole induction and shows no observable dip (Hare and Welsh 1958).

1.4 Spectral Density* at Zero Frequency

Consider a binary mixture of inert gases in thermal equilibrium, in which one species, A, is dilute enough so that the gas can be treated as a single molecule, A_1, moving in a cloud of B molecules. As mentioned previously, the negative correlation in the force pulses experienced by the particular molecule A_1, is strong enough so that the spectral density of the total force dips to zero, at zero frequency. This spectral density of the total force can be shown to exhibit an ω^2 behavior for low ω (Van Kranendonk 1968). Let the total force on A_1 at time t be $\vec{f}(t)$, and let $\vec{v}(t)$ be its velocity at time t. Then the force and velocity autocorrelation

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*In this thesis we will use the terms spectral density, (reduced) line shape function and power spectrum (of the induced dipole moment) interchangably.

functions are

$$\langle \vec{f}(t) \cdot \vec{f}(t + \tau) \rangle \qquad (1.2)$$

and

$$\langle \vec{v}(t) \cdot \vec{v}(t + \tau) \rangle \qquad (1.3)$$

respectively, where <...> denotes an average over time t. Using Newton's laws we obtain

$$\frac{d^2}{d\tau^2} \langle \vec{v}(t) \cdot \vec{v}(t + \tau) \rangle = \frac{1}{m} \frac{d}{d\tau} \langle \vec{v}(t) \cdot \vec{f}(t + \tau) \rangle \qquad (1.4)$$

As the system is in equilibrium, $\vec{v}(t)$ and $\vec{f}(t)$ are stationary, so we have

$$\langle \vec{v}(t) \cdot \vec{f}(t + \tau) \rangle = \langle \vec{v}(t - \tau) \cdot \vec{f}(t) \rangle \qquad (1.5)$$

Substitution of (1.5) into (1.4) gives

$$\begin{aligned} \frac{d^2}{d\tau^2} \langle \vec{v}(t) \cdot \vec{v}(t + \tau) \rangle &= \frac{1}{m} \frac{d}{d\tau} \langle \vec{v}(t - \tau) \cdot \vec{f}(t) \rangle \\ &= -\frac{1}{m^2} \langle \vec{f}(t - \tau) \cdot \vec{f}(t) \rangle \qquad (1.6) \end{aligned}$$

or

$$\frac{d^2}{d\tau^2} \langle \vec{v}(t) \cdot \vec{v}(t + \tau) \rangle = \frac{1}{m^2} \langle \vec{f}(t) \cdot \vec{f}(t + \tau) \rangle \qquad (1.7)$$

using the stationary property again. We now have an equation, (1.7), relating the force and velocity autocorrelation functions. Taking the Fourier transform of (1.7) we obtain

$$W_f(\omega) = m^2 \omega^2 W_v(\omega) \qquad (1.8)$$

where $W_f(\omega)$ and $W_v(\omega)$ are the force and velocity spectral densities respectively. $W_v(\omega)$ at zero frequency is proportional to the diffusion coefficient D, of molecule A_1 (Zwanzig 1963). Thus, at low frequency, the behavior of $W_f(\omega)$ is given accurately by

$$W_f(\omega) = 6m^2\omega^2 D \qquad (1.9)$$

Then if the diffusion coefficient, D, of molecule A_1 is finite, the spectral density of the total force dips to zero, at zero frequency. In consequence, if the induced dipole moment $\vec{\mu}(\vec{R})$ is proportional to the intermolecular force $\vec{f}(\vec{R})$, the spectral density of the total induced dipole moment will show the same ω^2 behavior at low ω, and hence the dip will extend to zero at zero frequency.

The above result is also true for finite concentrations (Van Kranendonk 1968, especially the 8th reference therein). Consider a gas with constituents A and B, with the number of molecules denoted N_A and N_B respectively. The masses of molecules of species A and B are m_A and m_B respectively. We denote by $\vec{\mu}_{AB}^{(ab)}(t)$, the dipole moment induced in molecule b of species B by molecule a of species A, and denote by $\vec{f}_{AB}^{(ab)}(t)$ the intermolecular force between this pair. Similarly $\vec{f}_{AA}^{(aa')}(t)$ and $\vec{f}_{BB}^{(bb')}(t)$ are the forces between two A molecules, a and a', and between two B molecules, b and b', respectively. Then we have for the force on a molecule a of species A at time t

$$m_A \dot{\vec{v}}_{Aa}(t) = \sum_{k=1}^{N_A} \vec{f}_{AA}^{(ak)}(t) + \sum_{b=1}^{N_B} \vec{f}_{AB}^{(ab)}(t) \qquad (1.10)$$

where we introduce the convention that

$$\vec{f}_{AA}^{(aa)}(t) = \vec{f}_{BB}^{(bb)}(t) = 0$$

Summing (1.10) over all molecules of species A we obtain

$$m_A \sum_{a=1}^{N_A} \dot{\vec{v}}_{Aa}(t) = \sum_{a=1}^{N_A} \sum_{k=1}^{N_A} \vec{f}_{AA}^{(ak)}(t) + \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{f}_{AB}^{(ab)}(t)$$

As $\vec{f}_{AA}^{(ak)}(t) = -\vec{f}_{AA}^{(ka)}(t)$, the first sum on the right-hand side of the above equation is identically zero. Hence we obtain

$$\sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{f}_{AB}^{(ab)}(t) = m_A \sum_{a=1}^{N_A} \dot{\vec{v}}_{Aa}(t). \qquad (1.11)$$

Now if the dipole moment induced in an AB pair were exactly proportional to the intermolecular force between the components of the pair, i.e. if

$$\vec{\mu}_{AB}^{(ab)}(t) = \vec{f}_{AB}^{(ab)}(t) \qquad (1.12)$$

suppressing the coefficient of proportionality for convenience, then the total induced dipole moment would be

$$\vec{M}(t) = \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}_{AB}^{(ab)}(t) = \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{f}_{AB}^{(ab)}(t).$$

Using (1.11) above, this reduces to

$$\vec{M}(t) = m_A \sum_{a=1}^{N_A} \dot{\vec{v}}_{Aa}(t) \qquad (1.13)$$

This is subject to the approximation that the intermolecular forces and induced dipole moments are pairwise additive. Pairwise additivity is known to be a good approximation, although it is not exact (Reed and Gubbins 1973; Van Kranendonk 1957).

Equation (1.13) shows that, given pairwise additivity of forces and induced dipole moments, and the assumed proportionality (1.12), the total induced dipole moment is proportional to the total force on the center of mass of the A (or of the B) molecules.

As shown above, the fact that the velocity of a molecule of species A is stationary in equilibrium is responsible for the intercollisional interference dip extending to zero, assuming (1.12), in the case that A is infinitely dilute. Similarly, for AB mixtures of arbitrary concentration, the fact that the center of mass velocity of the A molecules is stationary will also cause the intercollisional interference dip to extend to zero, under the assumption of (1.12). This we will now show in detail, following Lewis (1982).

From (1.13) we have

$$\vec{M}(t) \cdot \vec{M}(t + \tau) = m_A^2 \sum_{a=1}^{N_A} \sum_{a'=1}^{N_A} \dot{\vec{v}}_{Aa}(t) \cdot \dot{\vec{v}}_{Aa'}(t + \tau) \qquad (1.14)$$

Hence the autocorrelation function of the total induced dipole moment is given by

$$\begin{aligned} C(\tau) &\equiv \langle \vec{M}(t) \cdot \dot{\vec{M}}(t + \tau) \rangle \\ &= m_A^2 \{ N_A \langle \dot{\vec{v}}_{A1}(t) \cdot \dot{\vec{v}}_{A1}(t + \tau) \rangle \\ &+ \frac{N_A(N_A-1)}{2} [\langle \dot{\vec{v}}_{A1}(t) \cdot \dot{\vec{v}}_{A2}(t + \tau) \rangle \\ &+ \langle \dot{\vec{v}}_{A1}(t + \tau) \cdot \dot{\vec{v}}_{A2}(t) \rangle] \} \end{aligned} \tag{1.15}$$

as all A molecules are equivalent.

Now

$$\begin{aligned} \langle \dot{\vec{v}}_{Ai}(t) \cdot \dot{\vec{v}}_{Aj}(t + \tau) \rangle &= \frac{d}{d\tau} \langle \dot{\vec{v}}_{Ai}(t) \cdot \vec{v}_{Aj}(t + \tau) \rangle \\ &= \frac{d}{d\tau} \langle \dot{\vec{v}}_{Ai}(t - \tau) \cdot \vec{v}_{Aj}(t) \rangle \end{aligned}$$

by the stationary property of $\vec{v}_{Ai}(t)$, and this equals

$$\begin{aligned} &-\frac{d^2}{d\tau^2} \langle \vec{v}_{Ai}(t - \tau) \cdot \vec{v}_{Aj}(t) \rangle \\ &= -\frac{d^2}{d\tau^2} \langle \vec{v}_{Ai}(t) \cdot \vec{v}_{Aj}(t + \tau) \rangle \end{aligned}$$

again using the stationary property of $\vec{v}_{Ai}(t)$.

Hence, taking the Fourier transforms of both sides of (1.15), we find that the spectral density of the total induced dipole moment can be written as

$$W(\omega) = \omega^2 \{ m_A^2 \; N_A \, V_A^{(11)}(\omega) + m_A^2 \, N_A(N_A-1) \, \mathrm{Re} \, V_A^{(12)}(\omega) \} \tag{1.16}$$

where

$$V_A^{(ij)}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \langle \vec{v}_{Ai}(t) \cdot \vec{v}_{Aj}(t + \tau) \rangle \, dt \tag{1.17}$$

For an isolated system $\vec{v}_{Ai}(t)$ is bounded and will greatly exceed the mean thermal velocity only with very low probability. The correlation function $<\vec{v}_{Ai}(t)\cdot\vec{v}_{Aj}(t+\tau)>$ in three dimensions will then show, at worst, a weak $\tau^{-3/2}$ tail (Cohen 1975), so that the Fourier transforms $V_A^{(ij)}(\omega)$ will be finite for small ω. Hence, because of the ω^2 factor, $w(\omega)$ will go to zero as the frequency approaches zero. This is assuming of course, the proportionality of the intermolecular force and the induced dipole moment.

We note that an alternative expression for $w(\omega)$ of the same form as (1.16), but in terms of m_B, N_B and $\vec{v}_{Bi}(t)$ can be derived in the same way as (1.16).

The behavior of the spectral density shown above, for arbitrary concentrations, can be understood by considering two molecules of species A, A_1 and A_2, moving in a gas of B molecules. A collision of A_1 with A_2 ruins the correlation between the dipole moments induced in the B molecules by A_1 in the collisions immediately before and immediately after the collision with A_2. Initially one might expect that this effect, caused by an increase in concentration of species A, will lead to a reduction of the depth of the dip in the spectral density. However, there now exists an additional correlation between the dipole moments induced by A_1 and A_2 in their collisions with B molecules immediately following the A_1A_2 collision. After the A_1A_2 collision, A_1 and A_2 will tend to move in opposite directions, and hence the dipole moments induced by these two molecules in their next collisions will, on the average, be in opposite directions. This additional correlation tends to compensate for the lost correlation above, so that the relative concentration of the mixture will not reduce the depth of the dip in the spectral density at zero frequency.

1.5 Kinetic Theory of Intercollisional Interference

The line shape $w(\omega)$ of the dip at non-zero frequency has been studied by Van Kranendonk (1968). In obtaining his expressions for the intercollisional interference dip, he used the simplifying assumptions that only immediately successive collisions are correlated, that the induced dipole moment shows the same R dependence as the intermolecular force, and that ternary and higher order collisions can be neglected. Lewis and Van Kranendonk (1972) developed a general kinetic theory of intercollisional interference effects for Lorentz gases dilute in one component in which the first two assumptions above were relaxed but the third retained. They considered a very light molecule moving in a gas of heavy perturbing molecules which is assumed to form a cloud of randomly distributed stationary scatterers. Correlations between all the collisions in the collision sequence of the light molecules were taken into account, with no special relation assumed between the dipole moment and the intermolecular force. They obtained expressions for the depth of the intercollisional interference dip and the shape of the intercollisional spectrum. The theory of Lewis and Van Kranendonk has successfully fit spectra obtained through computer simulation by Lewis and Tjon (1978). Intercollisional interference effects were simulated for a two-dimensional hard disk Lorentz gas at various densities. The theory correctly fit the spectra for low densities, but extensions to higher densities proved unsuccessful. In particular, the depth of the dip at low densities was correctly predicted; a result which had not been available from experiment at that point. The primary limitations of this theory are that since it is a kinetic theory, it is valid only for low densities, up to a few hundred amagat, and one constituent of the binary mixture must be of much smaller mass and much more dilute than the other constituent. Lewis (1972) extended this theory to include gases where the restriction on the relative masses of the molecules was relaxed. This theory improved significantly the agreement between theoretical and experimental curves for the intercollisional halfwidth as a function of density in the induced fundamental band of H_2-He mixtures (Mactaggart 1972). Similar curves were obtained with Ar, Kr, and Xe as perturbing gases, but since H_2 is much less massive than these atoms, the finite mass correction is quite small in comparison with experimental uncertainty. This theory however, retains the assumption that one of the constituents is much more dilute than the other. Since experiments in collision-induced absorption are not performed, in general, under highly dilute conditions, it is desirable to extend this theory to include binary mixtures of arbitrary concentration. This was attempted by Wong (1978), who derived expressions for intercollisional interference effects in binary rare-gas mixtures of arbitrary concentration. However, only correlations between immediately successive collisions were considered, and hence his results are limited to systems of very low density. It is the aim of this work to extend the theory of Lewis and Van Kranendonk to include binary mixtures of gases in which no assumptions are made about the relative masses and number densities of the constituents, and where correlations between all the collisions in a collision sequence of a molecule are considered.

1.6 Present Work

In Chapter 2, we develop a theory of intercollisional interference effects whose expressions are valid for arbitrary binary mixtures of rare gases, at low density. This theory is extended in Chapter 3, to include gases in which the number of constituents is arbitrary.

The entire collisional-induced spectrum can be calculated assuming that the intermolecular force and induced dipole moment are known. The dependence of the intercollisional spectrum on the parameters characterizing the system, such as concentration ratio (expressed as mole fraction), density and temperature can be obtained in principle from our general expressions. The evaluation of our general results requires a great deal of computation, which is probably not warranted by the present experimental data. After approximation, however, we obtain expressions for the intercollisional interference dip which are readily applicable. At this level of approximation our results constitute a generalization of the work of Van Kranendonk (1968) to arbitrary concentration ratios and to include persistance-of-velocity effects (as was done in TIIE 2*). In particular, our theory is most useful in the calculation of $W(\omega)$ at low frequencies where the interference is greatest. We obtain the dependence of the halfwidth of the intercollisional spectrum on the concentration ratio for several binary rare-gas mixtures in section 2.7. The relative line shape as a function of $n_A n_B$ for Ar-Xe and Ne-Xe mixtures has been plotted in section 2.8. These curves were calculated at 2.3 cm^{-1} and 4.5 cm^{-1} for various number density ratios, n_A/n_B, to provide a comparison with experimental data obtained by Wong (1978).

In Chapter 2, the total dipole moment induced by a particular molecule a of species A, $\vec{\mu}^{(a)}(t)$, is treated as a time series consisting of a series of randomly occurring pulses $a_k\vec{\mu}_k(t-t_k)$, where $\vec{\mu}_k(t-t_k)$ is the dipole moment induced

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*TIIE 1-5 refers to a series of publications by Lewis and Van Kranendonk (1972) and Lewis (1972a, 1972b, 1973 and 1976).

in an AB collision in the k^{th} binary collision, and $a_k = \begin{matrix}0\\1\end{matrix}$ for $\begin{matrix}AA\\AB\end{matrix}$ collisions. The total dipole moment induced by a molecule b of species B is regarded in a similar way. We find that the reduced line shape function can be expressed as the sum of a pair of infinite series. The first series is due to the collision sequences of A molecules, where the $(n+1)^{th}$ term contains the correlation between an arbitrarily chosen initial collision of an A molecule and the n^{th} subsequent collision of that molecule. The second infinite series is defined similarly for B molecules. As in TIIE 2, these infinite series can be summed and $W(\omega)$ given in closed form (section 2.4). The evaluation of $W(\omega)$ requires the solution of two integral equations. The development of the theory in Chapter 3 is similar to that above, but the reduced line shape function is now expressed as the sum of n infinite series, where n is the number of species. Again, these series can be summed and $W(\omega)$ given in a closed expression, the evaluation of which requires the solution of n integral equations. The general evaluation of our closed expressions for $W(\omega)$ is difficult, and the major results of this thesis are obtained from a simplification of the expression for the line shape function in the binary mixture case. This simplification gives approximate solutions to the integral equations in explicit, closed form. A simplified form of the line shape function for a gas with an arbitrary number of species has been obtained, but application of even this reduced expression is not easy.

In Chapter 2, the reduced line shape function is dependent on the induced dipole moment via the time integrated dipole moment $\bar{\mu}(g,C)$, defined in section 2.4 for AB collisions. The dependence on the intermolecular force arises through the collisional probability distributions $P(g,\xi,c_1'|c_1)$, defined in section 2.4, for all possible types of collisions, AA, AB, BA, and BB collisions. We do not evaluate these quantities explicitly as they are computationally difficult, even for simple physical models (TIIE 2). In Chapter 3, the dependence on the induced dipole moments and the intermolecular forces arises in a similar fashion, but there are now more terms to take into account. We must consider the time integrated dipole moment $\bar{\mu}(g,C)$ for all the different dipole inducing binary collisions, AB, AC, BC collisions, etc. In addition, if there are n species present, the number of collisional probability distributions $P(g,\xi,c_1'|c_1)$ to account for is n^2.

In section 2.5, we prove that intercollisional interference in absorption by binary mixtures is always destructive at zero frequency. In section 2.6, we develop a simplified expression for the reduced line shape function. This simplification is achieved by approximating the quantity $\Delta(c_1'|c_1)$, defined in section 2.4, by an average value $\tilde{\Delta}\delta(c_1'-c_1)$ as was first considered in TIIE 2. The solutions to the integral equations, required for the evaluation of the expression for $W(\omega)$, can then be readily expressed in closed form. The resulting simplified expression was then used to obtain, in section 2.7, the line shape of the intercollisional spectrum and the dependence of the intercollisional spectrum on the concentration ratio of the mixture, and in section 2.8, the dependence of the line shape on $n_A n_B$ at low frequencies. The latter result was calculated specifically to compare with the experimental data and the theoretical curves fitted to that data by Wong (1978). Satisfactory agreement in most cases was obtained up to $n_A n_B = 5{,}000$ Am^2, but serious discrepancies exist beyond that point. We note that while the theoretical expression of Wong fits the data well up to 10,000 Am^2, this expression cannot be considered generally valid at lower frequencies as it yields a negative line shape (section 2.8).

CHAPTER 2

Theory of Intercollisional Interference in Translational Absorption by Binary Gas Mixtures

2.1 Introduction

A theory of intercollisional interference effects is developed in this chapter for arbitrary binary rare-gas mixtures. That is, we will be dealing with translational absorption in a binary mixture of gases, in which the mass ratio, m_B/m_A, and the number density ratio, n_B/n_A, between the two constituents is arbitrary. Repeated reference will be made to the theory of Lewis and Van Kranendonk (1972) and later extensions of this theory by Lewis (1972a, 1972b, 1973, 1976). For convenience, this series of publications will be denoted by the abbreviation TIIE 1-5 (for "Theory of Intercollisional Interference Effects"). Following TIIE 1-5, we will assume that unlike molecules interact through pairwise additive central forces, and that the induced dipole moments are pairwise additive and instantaneously parallel to these forces. The assumption that $\tau_c >> \tau_d$ will be made, so that only low densities will be considered. Ternary and higher order collisions can then be neglected, and a temporal superposition for the dipole moments induced in isolated binary collisions can be used to represent the total induced dipole moment in a particular molecule. A brief discussion regarding the underlying principles upon which our calculations are based is given in section 1 of TIIE 1.

In this work we will consider the (reduced) line shape function $W(\omega)$, rather than study the absorption coefficient per wavelength in vacuo, $\tilde{A}(\omega)$, directly. The (reduced) line shape function $W(\omega)$ for translational spectra, is related to the absorption coefficient $\tilde{A}(\omega)$ through

$$\tilde{A}(\omega) = 2\tilde{\kappa}\frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}} W(\omega) \qquad (2.1)$$

where $\tilde{\kappa} = 8\pi^3/3\hbar V$

and $$W(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau} C(\tau)\, d\tau \qquad (2.2)$$

is the Fourier transform of the autocorrelation function $C(\tau)$ of the total induced dipole moment $\vec{M}(t)$, following TIIE 1. That is, $W(\omega)$ is the power spectrum of $\vec{M}(t)$. In the classical approximation

$$C(\tau) = \langle\vec{M}(t) \cdot \vec{M}(t + \tau)\rangle \qquad (2.3)$$

where <...> denotes a time average, again following TIIE 1.

2.2 General Theory

To derive an expression for $W(\omega)$, we first consider the dipole moment autocorrelation function $C(\tau)$. The total induced dipole moment in a volume V, containing N_A molecules of species A and N_B molecules of species B is $\vec{M}(t)$, and can be written as a sum of dipole moments induced in AB pairs

$$\vec{M}(t) = \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \qquad (2.4)$$

where $\vec{\mu}^{(ab)}(t)$ is the dipole moment induced by the interaction between molecule a of species A, and molecule b of species B. Then from (2.3) we have

$$C(\tau) = \langle \sum_{a,a'=1}^{N_A} \sum_{b,b'=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b')}(t+\tau) \rangle \qquad (2.5)$$

$$= \langle \sum_{a=1}^{N_A} \sum_{b,b'=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab')}(t+\tau)$$

$$+ \sum_{a,a'=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b)}(t+\tau)$$

$$- \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t+\tau)$$

$$+ \sum_{\substack{a,a' \\ a'\neq a}}^{N_A} \sum_{\substack{b,b' \\ b'\neq b}}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b')}(t+\tau) \rangle \quad . \qquad (2.6)$$

The third term in (2.6) is subtracted since it is counted in both the first and second term of (2.6), but only occurs once in (2.5). It is a purely intracollisional term, expressing the correlation between collisions of the same two molecules. The fourth term in (2.6) expresses the correlation between collisions in which no molecule is common. This term is expected to be small for low densities and will be neglected.

Let the dipole moment induced by a molecule a of species A in all other molecules at time t be $\vec{\mu}^{(a)}(t)$. We can write

$$\vec{\mu}^{(a)}(t) = \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \ . \tag{2.7}$$

Similarly

$$\vec{\mu}^{(b)}(t) = \sum_{a=1}^{N_A} \vec{\mu}^{(ab)}(t) \tag{2.8}$$

where $\vec{\mu}^{(b)}(t)$ is the dipole moment induced by a molecule b of species B in all other molecules at time t. Neglecting the final term in (2.6) we have

$$C(\tau) = < \sum_{a=1}^{N_A} \sum_{b,b'=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab')}(t+\tau)$$

$$+ \sum_{a,a'=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b)}(t+\tau)$$

$$- \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t+\tau)>$$

Using (2.7) and (2.8) this reduces to

$$C(\tau) = < \sum_{a=1}^{N_A} \vec{\mu}^{(a)}(t) \cdot \vec{\mu}^{(a)}(t+\tau)$$

$$+ \sum_{b=1}^{N_B} \vec{\mu}^{(b)}(t) \cdot \vec{\mu}^{(b)}(t+\tau)$$

$$- \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t+\tau)> \ .$$

Since all molecules of species A are equivalent, as are all molecules of species B, we have

$$C(\tau) = N_A \langle \vec{\mu}^{(a)}(t) \cdot \vec{\mu}^{(a)}(t + \tau) \rangle$$

$$+ N_B \langle \vec{\mu}^{(b)}(t) \cdot \vec{\mu}^{(b)}(t + \tau) \rangle$$

$$+ \langle \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t + \tau) \rangle \quad . \tag{2.9}$$

At low densities we can write the pure intracollisional term, in the temporal superposition approximation (TIIE 1), as

$$\langle \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t + \tau) \rangle$$

$$= \mathcal{N}_{AB} \cdot V \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) \rangle_i \tag{2.10}$$

where $\langle \ldots \rangle_i$ denotes the collisional average of the dipole moments induced in AB collisions over all AB collisions, and $\mathcal{N}_{AB}$ is the total number of AB collisions per unit volume V per unit time, and is described along with related quantities in detail below.

2.3 Collisional Frequencies

Consider a binary mixture of gases in thermal equilibrium at temperature T, with constituents A and B, with number densities and masses denoted n_A, m_A and n_B, m_B

respectively. If Σ_{AA}, Σ_{AB}, Σ_{BA} and Σ_{BB} are the total scattering cross sections for AA, AB, BA, and BB collisions respectively, then the three dimensional collision frequencies per unit volume are

$$N_{AB} = N_{BA} = 2n_A n_B \Sigma_{AB} \sqrt{2kTm_o/\pi m_A m_B}$$

$$N_{AA}/2 \text{ where } N_{AA} = 4n_A^2 \Sigma_{AA} \sqrt{kT/\pi m_A}$$

$$N_{BB}/2 \text{ where } N_{BB} = 4n_B^2 \Sigma_{BB} \sqrt{kT/\pi m_B}$$

where $m_o = m_A + m_B$, and k is Boltzmann's constant (Chapman and Cowling 1970).

Now, the collision frequency of a single A molecule with both A and B molecules, denoted ν_A, is

$$\nu_A = (N_{AA} + N_{AB})/n_A$$

$$= n_A S_A + n_B S_{AB}$$

where

$$S_A = 4\Sigma_{AA} \sqrt{kT/\pi m_A}$$

$$S_{AB} = 2\Sigma_{AB} \sqrt{2kTm_o/\pi m_A m_B}$$

$$S_B = 4\Sigma_{BB} \sqrt{kT/\pi m_B} .$$

Similarly

$$\nu_B = n_A S_{AB} + n_B S_B$$

We denote the relative frequencies of AA and AB collisions in the collision history of a molecule of species A by u_{AA} and u_{AB} respectively, and similarly denote by u_{BB} and u_{BA} the relative frequencies of BB and BA collisions in the collision history of a molecule of species B. Then clearly

$$u_{AA} = N_{AA}/(N_{AA} + N_{AB}) \; ; \; u_{AB} = N_{AB}/(N_{AA} + N_{AB})$$

and

$$u_{BB} = N_{BB}/(N_{BA} + N_{BB}) \; ; \; u_{BA} = N_{BA}/(N_{BA} + N_{BB}) .$$

2.4 Continuation of General Theory

The dipole moment autocorrelation function can be written as

$$\begin{aligned} C(\tau)/V = {} & n_A \langle \vec{\mu}^{(a)}(t) \cdot \vec{\mu}^{(a)}(t+\tau) \rangle \\ & + n_B \langle \vec{\mu}^{(b)}(t) \cdot \vec{\mu}^{(b)}(t+\tau) \rangle \\ & - N_{AB} \langle \mu_i(t) \cdot \mu_i(t+\tau) \rangle_i \end{aligned} \tag{2.11}$$

from (2.10). We will now use a temporal superposition approximation for the dipole moments induced in isolated binary collisions to represent the total induced dipole moment in a particular molecule i.e.

$$\vec{\mu}^{(a)}(t) = \sum_i a_i \vec{\mu}_i(t - t_i)$$

where

$$\alpha_i = 1 \text{ for AB collisions}$$
$$= 0 \text{ for AA collisions}$$

similarly for $\vec{\mu}^{(b)}(t)$. We then obtain

$$\begin{aligned} C(\tau)/V = {} & n_A < \sum_{i,j} \alpha_i \vec{\mu}_i(t - t_i) \cdot \alpha_j \vec{\mu}_j(t + \tau - t_j) > \\ & + n_B < \sum_{k;q} \alpha_k \vec{\mu}_k(t - t_k) \cdot \alpha_q \vec{\mu}_q(t + \tau - t_q) > \\ & - N_{AB} < \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) >_i \end{aligned} \qquad (2.12).$$

Taking out the intracollisional terms we obtain

$$\begin{aligned} C(\tau)_{\text{intra}}/V = {} & n_A < \sum_i \alpha_i^2 \vec{\mu}_i(t - t_i) \cdot \vec{\mu}_i(t + \tau - t_i) > \\ & + n_B < \sum_k \alpha_k^2 \vec{\mu}_k(t - t_k) \cdot \vec{\mu}_k(t + \tau - t_k) \\ & - N_{AB} < \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) >_i \\ = {} & n_A \nu_A < \alpha_i^2 \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) >_i \\ & + n_B \nu_B < \alpha_k^2 \vec{\mu}_k(t) \cdot \vec{\mu}_k(t + \tau) >_k \\ & - N_{AB} < \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) >_i \end{aligned} \qquad (2.13)$$

where ν_A, and ν_B are as defined in section 2.3. In the first term in (2.13), $<\ldots>_i$ denotes the collisional average over all collisions involving molecule a of species A. The fraction of the coefficients a_i^2 that are non-zero is then given by u_{AB}, whigh is the relative frequency of AB collisions in the collision history of a molecule of species A, and is defined in section 2.3. Similarly, in the second term of (2.13), the fraction of the coefficients a_k^2 that are non-zero is given by u_{BA}. Consequently we obtain

$$C(\tau)_{\text{intra}}/V = (n_A \nu_A u_{AB} + n_B \nu_B u_{BA} - N_{AB}) \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t+\tau) \rangle_i$$

for the intracollisional autocorrelation function, where $\langle \ldots \rangle_i$ denotes a collisional average over AB collisions. This reduces to

$$C(\tau)_{\text{intra}}/V = N_{AB} \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t+\tau) \rangle_i \quad . \qquad (2.14)$$

We will now consider the intercollisional terms in (2.12),

$$C(\tau)_{\text{inter}}/V = n_A \langle \sum_{\substack{i,j \\ i \neq j}} a_i \vec{\mu}_i(t - t_i) \cdot a_j \vec{\mu}_j(t + \tau - t_j) \rangle$$

$$+ n_B \langle \sum_{\substack{k,q \\ k \neq q}} a_k \vec{\mu}_k(t - t_k) \cdot a_q \vec{\mu}_q(t + \tau - t_q) \rangle \qquad (2.15)$$

This can be rearranged into the sum of two series, the nth terms of which express the correlation between the ith and the (i+n)th collisions:

$$C(\tau)_{\text{inter}}/V = n_A \sum_{n=1}^{\infty} C_n^A(\tau) + n_B \sum_{n=1}^{\infty} C_n^B(\tau) \qquad (2.16)$$

where

$$C_n^A(\tau) = \langle \sum_i [\alpha_i \vec{\mu}_i(t - t_i) \cdot \alpha_{i+n} \vec{\mu}_{i+n}(t + \tau - t_{i+n})$$

$$+ \alpha_{i+n} \vec{\mu}_{i+n}(t - t_{i+n}) \cdot \alpha_i \vec{\mu}_i(t + \tau - t_i)] \rangle, \qquad (2.17)$$

and similarly for $C_n^B(\tau)$.

We introduce the variable $x_i = t_{i+1} - t_i > 0$, for the interval between two successive collisions, and use a time average in the above expressions;

$$\text{i.e.} \quad \langle f \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T f(t)\,dt \quad .$$

Then (2.17) becomes

$$C_n^A(\tau) = \lim_{T\to\infty} \frac{1}{T} \sum_i [C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau)$$

$$+ C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} + \tau)] \qquad (2.18)$$

with

$$C^A_{i,i+n}(\tau) = \int_{-\infty}^{\infty} \alpha_i \vec{\mu}_i(t) \cdot \alpha_{i+n} \vec{\mu}_{i+n}(t - \tau)\,dt \qquad (2.18')$$

where the i's refer to the collision variables of a molecule of species A. Similar expressions hold for $C_n^B(\tau)$.

The expression on the right hand side of (2.18) is equal to the average collision frequency ν_A, multiplied by the mean of the quantity in square brackets averaged over the time intervals $x_i, \ldots, x_{i+n-1}$ and over the collision variables $i, \ldots, i+n$. We denote the average value of $C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau)$ over the collision variables by

$$\langle C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau)\rangle_i \, .$$

Then

$$\begin{aligned} C^A_n(\tau) = \nu_A \int_0^\infty \cdots \int_0^\infty & p(x_i, \ldots, x_{i+n-1}) \\ & \times [\langle C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau)\rangle_i \\ & + \langle C^A_{i,i+n}(x_i + \ldots + x_{i+n-1} + \tau)\rangle_i]\, dx_i \ldots dx_{i+n-1} \end{aligned} \tag{2.19}$$

where $p(x_i, \ldots, x_{i+n-1})$ is the distribution of the collision intervals $x_i, \ldots, x_{i+n-1}$. From (2.16) and (2.2) we obtain

$$W(\omega)_{inter}/V = n_A \sum_{n=1}^\infty W^A_n(\omega) + n_B \sum_{n=1}^\infty W^B_n(\omega) \tag{2.20}$$

where

$$W^A_n(\omega) = \int_{-\infty}^\infty e^{i\omega\tau} C^A_n(\tau)\, d\tau \tag{2.21}$$

with a similar expression for $W^B_n(\omega)$.

We will now evaluate the quantities $W^A_n(\omega)$ and $W^B_n(\omega)$ appearing in (2.20) and sum the series to obtain a closed expression for the intercollisional line shape function per unit volume, $W(\omega)_{inter}/V$.

To evaluate $W_n^A(\omega)$, we follow a molecule of species A, and consider all possible non-zero collision sequences for a given n. If n=1, then the only non-zero collision sequence is the molecule of species A undergoing two successive collisions with molecules of species B (see Figure 2.1)

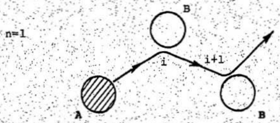

Figure 2.1. Collision sequence of a molecule of species A for n=1.

Then from the defining equation for $C_n^A(\tau)$, (2.19), and (2.21) we obtain

$$W_1^A(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\, \nu_A \int_0^{\infty} p_{AB}(x_i) \times [<\int_{-\infty}^{\infty} a_i\vec{\mu}_i(t)\cdot a_{i+1}\vec{\mu}_{i+1}(t - x_i + \tau)\, dt>_i + <\int_{-\infty}^{\infty} a_i\vec{\mu}_i(t)\cdot a_{i+1}\vec{\mu}_{i+1}(t - x_i - \tau)\, dt>_i]dx_i\, d\tau. \tag{2.22}$$

We note that the distribution of collision intervals $p(x_i)$

appearing in (2.19) has now become $p_{AB}(x_i)$, denoting the distribution for AB collisions. The above equation reduces to

$$W_1^A(\omega) = 2\nu_A \int_0^\infty p_{AB}(x_i)\, e^{-i\omega x_i}\, dx_i$$

$$\times \langle a_i \vec{\mu}_i(\omega) \cdot a_{i+1}\, \vec{\mu}_{i+1}(-\omega)\rangle_i \tag{2.23}$$

where

$$\vec{\mu}_i(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau} \vec{\mu}_i(\tau)\, d\tau$$

Since the collision sequence is an A molecule undergoing two successive collisions with B molecules, the fraction of the coefficient $a_i a_{i+1}$ that is non-zero is u_{AB}^2. Letting

$$\tilde{p}_{AB}(\omega) = \int_0^\infty p_{AB}(x_i)\, e^{-i\omega x_i}\, dx_i \tag{2.24}$$

we obtain

$$W_1^A(\omega) = 2\nu_A u_{AB}^2 \,\mathrm{Re}\, [\tilde{p}_{AB}(\omega) \langle \vec{\mu}_i(\omega) \cdot \vec{\mu}_{i+1}(-\omega)\rangle_i] \tag{2.25}$$

We will now use the approximation

$$\vec{\mu}(t) = \sum_i \overline{\vec{\mu}}_i\, \delta(t - t_i) \tag{2.26}$$

where δ is the Dirac delta function. This approximation is valid for low frequencies, but is inapplicable at high frequencies (TIIE 1). It is equivalent to assuming that in the calculation of the intercollisional spectrum at low densities, one can replace $\vec{\mu}_i(\omega)$ by its value at $\omega=0$, which is denoted $\bar{\vec{\mu}}_i$. Following TIIE 1,

$$\vec{\mu}_i(\omega) \approx \vec{\mu}_i(0) = \int_{-\infty}^{\infty} \vec{\mu}_i(\tau)\, d\tau = \bar{\vec{\mu}}_i \ . \qquad (2.27)$$

The effect of the frequency dependence of $\vec{\mu}_i(\omega)$ on the line shape function is discussed in section 6 of TIIE 1. Using (2.27) in (2.25) we obtain

$$W_1^A(\omega) = 2\nu_A\ u_{AB}^2\ \mathrm{Re}\ [\tilde{p}_{AB}(\omega)\ \langle\bar{\vec{\mu}}_i \cdot \bar{\vec{\mu}}_{i+1}\rangle_i] \qquad (2.28)$$

In evaluating the correlation coefficient $\langle\bar{\vec{\mu}}_i \cdot \bar{\vec{\mu}}_{i+1}\rangle_i$ we will follow TIIE 2. We will first consider the general case of $\langle\bar{\vec{\mu}}_i \cdot \bar{\vec{\mu}}_{i+n}\rangle_i$, then set $n=1$ to obtain the coefficient in (2.28). Eight quantities are required to characterize a binary collision between spherically symmetric molecules with no internal degrees of freedom. The most convenient choice of parameters for collisional averaging is

$$\{\vec{c}_1,\ c_1',\ \xi,\ \phi,\ g,\ \phi_g\} \qquad (2.29)$$

where there is an additional discrete index s required if the intermolecular force has an attractive part (TIIE 2). In the above set, $\vec{c}_1$ is the velocity of molecule 1 before the collision, $(c_1',\ \xi,\ \phi)$ are the spherical polar coordinates of the velocity of molecule 1 after the collision in a coordinate system with the z-axis along $\vec{c}_1$, $g = |g_{12}| = |\vec{c}_2 - \vec{c}_1|$, and ϕ_g is the azimuth of $\vec{g}_{12}$ in a coordinate system with the x-axis along $\vec{C} = \vec{c}_1{}' - \vec{c}_1$ (see Figure 2.2)

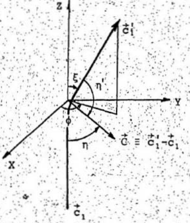

Figure 2.2 Collision variables and related quantities.

The set (2.29) has been shown to be equivalent to the standard set of collision variables $\{b, \varepsilon, \vec{c}_1, \vec{c}_2\}$ in TIIE 2. Also, it has been pointed out in TIIE 2 that a knowledge of C and g is equivalent to a knowledge of b and g.

The projection of the time integrated dipole moment $\bar{\vec{\mu}}$ induced by a collision characterized by $\{b, \varepsilon, \vec{c}_1, \vec{c}_2\}$ on the apse line is completely determined by b and g, and hence by C and g, according to our assumptions about the intermolecular force and induced dipole moment $\bar{\mu}$. Therefore, we write this projection as $\overline{\mu}(g,C)$. The time integrated dipole moment $\overline{\vec{\mu}}$ appearing in (2.28) is parallel to the unit vector $\hat{C}$ along the apse line

$$\overline{\vec{\mu}}(g,\vec{C}) = \vec{\mu}(g,C)\hat{C} \ .$$

Since $\vec{C} \equiv \vec{c}_1^{\,\prime} - \vec{c}_1$ is completely determined by the subset $(c_1, c_1^{\prime}, \xi, \phi)$ of the set of collision variables (2.29), $\overline{\vec{\mu}}$ is independent of the azimuth ϕ_g. In addition, the azimuth ϕ of $\vec{c}_1^{\,\prime}$, $\vec{C}$ and $\overline{\vec{\mu}}$ is uniformly distributed about $\vec{c}_1$. As a result, we only need the conditional probability distribution $P(g, \xi, c_1^{\prime}|c_1)$ of g, ξ and $c_1^{\prime}$ for a given c_1, and the distribution of $\vec{c}_1$, $P(\vec{c}_1)$, to evaluate the correlation coefficient $\langle\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+n}\rangle_i$. The full conditional probability distribution of the set (2.29) is not required. The distributions $P(g, \xi, c_1^{\prime}|\vec{c}_1)$ and $P(\vec{c}_1)$ are related to the distributions $P(g, \xi, c_1^{\prime}|c_1)$ and $P(c_1)$ by

$$P(g, \xi, c_1^{\prime}|c_1) = P(g, \xi, c_1^{\prime}|\vec{c}_1)$$

and

$$P(c_1) = 4\pi c_1^2 \ P(\vec{c}_1)$$

since the gas mixtures are isotropic. $P(c_1)$ is of course the Maxwell-Boltzmann distribution of speeds. In TIIE 2, since A is treated as infinitely dilute, $\langle\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+n}\rangle_i$ contains the correlation between a collision, i, of an A molecule with a B molecule, and a later collision, i+n, of the same A molecule with another B molecule. Therefore, the distributions that are required for the evaluation of $\langle\vec{\mu}_i \cdot \vec{\mu}_{i+n}\rangle_i$ are $P(g, \xi, c_1'|c_1)$ for AB collisions, and $P(c_1)$ for A molecules. In this work, since we are dealing with arbitrary concentrations of A and B molecules, we require the conditional probability distributions $P(g, \xi, c_1'|c_1)$ for all four possible types of collisions, AA, AB, BA, and BB collisions, and the distributions $P(c_1)$ for both A and B molecules. These different quantities will be denoted by the appropriate subscripts.

We denote the angles between $\vec{c}_1$ and $\vec{C}$, and $\vec{c}_1'$ and $\vec{C}$ by η and η' respectively. We take c_k to be the speed of molecule 1 before the k^{th} collision of the collision sequence i,...,i+n. However, the velocity of molecule 1 before and after a collision is still denoted by $\vec{c}_1$ and $\vec{c}_1'$ without reference to the position of the collision in the collision sequence.

The average of a random vector over its azimuthal angle is clearly a vector parallel to the axis which the azimuthal angle is defined, if that vector is uniformly distributed in its azimuth. The quantities $\vec{\mu}(g, \vec{c})$ and $\vec{c}_1'$ are uniformly distributed in their azimuth ϕ about $\vec{c}_1$ in terms of the set of collision variables (2.29). Thus, the average of $\vec{\mu}_{i+n}$

over all the variables of the $(i+n)^{th}$ collision except $\vec{c}_{i+n}$, is a vector parallel to c_{i+n} which is the defining axis for the azimuthal angle. The average of this vector over all the variables of the $(i+n-1)^{th}$ collision except $\vec{c}_{i+n-1}$ is a vector parallel to $\vec{c}_{i+n-1}$, and so forth. Thus, continuing in this way and following a collision sequence of an A molecule, $\langle\bar{\vec{\mu}}_i \cdot \bar{\vec{\mu}}_{i+n}\rangle_i$ can be expressed in terms of quantities defined for two collisions, an AA and an AB collision. The averaging process is shown schematically in Figure 2.3.

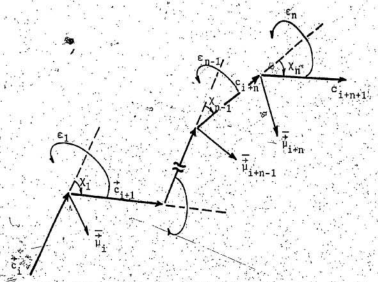

Figure 2.3 Collisional averaging.

If one follows a collision sequence of a B molecule, $\langle \vec{\bar{\mu}}_i \cdot \vec{\bar{\mu}}_{i+n} \rangle_i$ can be expressed in terms of quantities defined for a BB and a BA collision. First, we will follow a collision sequence of an A molecule. We will write the average of $\vec{\bar{\mu}}_{i+n}$ over all the collision variables of the $(i+n)^{th}$ collision except the velocity before the collision, $\vec{c}_{i+n}$, as

$$A_A(c_{i+n})\ \hat{c}_{i+n}$$

where $A_A(c_{i+n})$ is independent of $\hat{c}_{i+n}$. In terms of our collision variables this can be written as

$$\langle \vec{\bar{\mu}}(g, \vec{C}) \rangle_{c_1', \xi, \phi, g, \phi_g} = A_A(c_1)\ \hat{c}_1 \tag{2.30}$$

where

$$A_A(c_1) = \int_0^\infty dc_1'\ A_A(c_1'|c_1) \tag{2.31}$$

and

$$\begin{aligned} A_A(c_1'|c_1) &= \langle \vec{\bar{\mu}}(g, \vec{C}) \cdot \hat{c}_1 \rangle_{\xi, \phi, g, \phi_g} \\ &= \int_0^\pi d\xi \sin \xi \int_0^\infty dg\ \bar{\mu}(g, C) \cos \eta\ P_{AB}(g, \xi, c_1'|c_1) \end{aligned} \tag{2.32}$$

The subscript A on $A_A(c_1)$ and $A_A(c_1'|c_1)$ denotes the fact that we are following an A molecule, and the subscript AB on

$P_{AB}(g,\ \xi,\ c_1'|c_f)$ denotes the conditional distribution for AB collisions, since the final collision in a collision sequence of an A molecule is with a B molecule.

When (2.30) is averaged over all the variables of the $(i+n-1)^{th}$ collision except $\vec{c}_{i+n-1}$, we obtain

$$\hat{c}_{i+n-1} \int_0^\infty dc_{i+n}\ A_A(c_{i+n})\ \Delta_{AB}(c_{i+n}|c_{i+n-1})$$

or (2.33)

$$\hat{c}_{i+n-1} \int_0^\infty dc_{i+n}\ A_A(c_{i+n})\ \Delta_{AA}(c_{i+n}|c_{i+n-1})$$

depending upon whether the collision is with another A molecule or with a B molecule. In terms of our collision variables

$$\Delta_{\substack{AA\\AB}}(c_1'|c_1) = \langle \hat{c}_1 \cdot \hat{c}_1' \rangle_{\xi,\phi,g,\phi_g} = \int_0^\pi d\xi\ \sin\xi\ \cos\xi\ P_{\substack{AA\\AB}}(\xi,c_1'|c_1) \qquad (2.34)$$

and $P_{\substack{AA\\AB}}(\xi,c_1'|c_1)$ is the conditional distribution of ξ and c_1' for a given c_1 for $\substack{AA\\AB}$ collisions. The averaging process, continued for $\vec{\mu}_{i+n}$ over all the variables of the $(i+n)^{th}$ to $(i+2)^{th}$ collisions and over all the variables of the $(i+1)^{th}$ collision except $\vec{c}_{i+1}$, yields

$$\vec{c}_{i+1} \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_{i+2} \mathcal{A}_A(c_{i+n})$$

$$\times \Delta_{\substack{AA\\AB}}(c_{i+n}|c_{i+n-1}) \Delta_{\substack{AA\\AB}}(c_{i+n-1}|c_{i+n-2}) \cdots \Delta_{\substack{AA\\AB}}(c_{i+2}|c_{i+1}) \qquad (2.35)$$

The average of $u(c_1')\hat{c}_1' \cdot \overline{\vec{\mu}}(g,\vec{c})$ for some function u over all of the collision variables (2.29), including $\vec{c}_1$, is

$$\langle u(\vec{c}_1')\hat{c}_1 \cdot \overline{\vec{\mu}}(g,\vec{c})\rangle_{c_1,c_1',\varepsilon,\phi,g,\phi_g}$$

$$= \int_0^\infty dc_1\, P_A(c_1) \int_0^\infty dc_1'\, u(c_1')\, \mathcal{B}_A(c_1'|c_1) \quad , \qquad (2.36)$$

where $\mathcal{B}_A(c_1'|c_1) = \langle\overline{\vec{\mu}}(g,\vec{C}) \cdot \hat{c}_1'\rangle_{\xi,\phi,g,\phi_g}$

$$(2.37)$$

$$= \int_0^\pi d\xi \sin\xi \int_0^\infty dg\, \overline{u}(g,C) \cos\eta'\, P_{AB}(g,\xi,c_1'|c_1)$$

The subscript A on $\mathcal{B}_A(c_1'|c_1)$ denotes the fact that we are following an A molecule, and the subscript AB on $P_{AB}(g,\xi,c_1'|c_1)$ denotes the conditional distribution for AB collisions, since the first collision in a collision sequence of an A molecule is with a B molecule. We note that the expressions (2.32) and (2.37) for $\mathcal{A}_A(c_1'|c_1)$ and $\mathcal{B}_A(c_1'|c_1)$ differ only in the occurrence of cos η in the former and cos η' in the latter. These quantities are closely related by the Principle of

Detailed Balancing, as shown in TIIE 2.

We then have

$$\langle \vec{\mu}_i \cdot \vec{\mu}_{i+n} \rangle_i = \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i \, A_A(c_{i+n})$$

$$\times \Delta_{\substack{AA\\AB}}(c_{i+n}|c_{i+n-1}) \cdots \Delta_{\substack{AA\\AB}}(c_{i+2}|c_{i+1}) \, B_A(c_{i+1}|c_i) P_A(c_i) \quad (2.38)$$

for a collision sequence of an A molecule. It can be easily seen that if one follows a collision sequence of a B molecule, one obtains

$$\langle \vec{\mu}_i \cdot \vec{\mu}_{i+n} \rangle_i = \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i \, A_B(c_{i+n})$$

$$\times \Delta_{\substack{BB\\BA}}(c_{i+n}|c_{i+n-1}) \cdots \Delta_{\substack{BB\\BA}}(c_{i+2}|c_{i+1}) \, B_B(c_{i+1}|c_i) \, P_B(c_i) \quad (2.39)$$

where

$$A_B(c_1'|c_1) = \int_0^\pi d\xi \, \sin \xi \int_0^\infty dg \, \vec{\mu}(g,C) \cos \eta \, P_{BA}(g,\xi,c_1'|c_1) \quad (2.40)$$

and

$$\Delta_{\substack{BB\\BA}}(c_1'|c_1) = \int_0^\pi d\xi \, \sin \xi \, \cos \xi \, P_{\substack{BB\\BA}}(\xi,c_1'|c_1) \quad (2.41)$$

and

$$B_B(c_1'|c_1) = \int_0^\pi d\xi \, \sin\xi \int_0^\infty dg \, \bar{\mu}(g,C) \, \cos\eta' \, P_{BA}(g,\xi,c_1'|c_1) \qquad (2.42)$$

The quantities $A_B(c_1'|c_1)$ and $B_B(c_1'|c_1)$ are related in the same way as $A_A(c_1'|c_1)$ and $B_A(c_1'|c_1)$.

We have now obtained general expressions for the correlation coefficients $\langle\vec{\mu}_i \cdot \vec{\mu}_{i+n}\rangle_i$ following collision sequences of both A and B molecules. These results can now be used to obtain explicit expressions for $W_n^A(\omega)$ and $W_n^B(\omega)$. We recall the following expression, (2.28), for $W_1^A(\omega)$

$$W_1^A(\omega) = 2\nu_A \, u_{AB}^2 \, \mathrm{Re}[\tilde{p}_{AB}(\omega) \, \langle\vec{\mu}_i \cdot \vec{\mu}_{i+1}\rangle_i] \; .$$

Setting n=1 in (2.38), we obtain

$$W_1^A(\omega) = 2\nu_A \, u_{AB}^2 \, \mathrm{Re}[\tilde{p}_{AB}(\omega) \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times \, A_A(c_{i+1}) \, B_A(c_{i+1}|c_i) \, P_A(c_i)] \; . \qquad (2.43)$$

We will now consider $W_2^A(\omega)$. There are two non-zero collision sequences that an A molecule can undergo for n=2; (1) three successive collisions with B molecules, (2) a collision with a B molecule, followed by a collision with another A molecule, followed by a collision with a B molecule (see Figure 2.4).

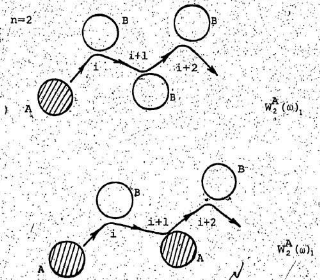

Figure 2.4 Collision sequences of a molecule of species A for n=2.

For the contribution to $W_2^A(\omega)$ from the first sequence, (1), which we denote $W_2^A(\omega)_1$, from (2.19) and (2.21) we obtain

$$W_2^A(\omega)_1 = \int_{-\infty}^{\infty} e^{i\omega\tau} d\tau \; \nu_A \int_0^{\infty}\int_0^{\infty} p_{AB}(x_i)\, p_{AB}(x_{i+1})$$

$$\times \Big[\Big< \int_{-\infty}^{\infty} \alpha_i \vec{\mu}_i(t) \cdot \alpha_{i+2}\, \vec{\mu}_{i+2}\,(t-x_i-x_{i+1}+\tau)\, dt \Big>_i$$

$$+ \Big< \int_{-\infty}^{\infty} \alpha_i \vec{\mu}_i(t) \cdot \alpha_{i+2}\, \vec{\mu}_{i+2}\,(t-x_i-x_{i+1}-\tau)\, dt \Big>_i \Big] dx_i\, dx_{i+1}$$

$$= 2\nu_A \mathrm{Re}[\tilde{p}^2_{AB}(\omega) \; \langle a_i \vec{\mu}_i(\omega) \cdot a_{i+2} \vec{\mu}_{i+2}(-\omega)\rangle_i]$$

$$= 2\nu_A \mathrm{Re}[\tilde{p}^2_{AB}(\omega) \; \langle a_i a_{i+2} \; \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}\rangle_i] \qquad (2.44)$$

The fraction of the coefficient $a_i a_{i+2}$ that is non-zero for this collision sequence is u^3_{AB}, so we have

$$W^A_2(\omega)_1 = 2\nu_A u^2_{AB} \; \mathrm{Re}[\tilde{p}^2_{AB}(\omega) \; u_{AB} \langle\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}\rangle_i] \qquad (2.45)$$

The correlation coefficient $\langle\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}\rangle_i$ can be obtained from (2.38) using the given collision sequence. We have

$$\langle\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}\rangle_i = \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i \, \mathcal{A}_A(c_{i+2})$$

$$\times \Delta_{AB}(c_{i+2}|c_{i+1}) \; \mathcal{B}_A(c_{i+1}|c_i) \; P_A(c_i) \qquad (2.46)$$

Then we can write (2.45) as

$$W^A_2(\omega)_1 = 2\nu_A \; u^2_{AB} \; \mathrm{Re}\,[\tilde{p}_{AB}(\omega) \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times \; \mathcal{A}_A(c_{i+2}) \; \tilde{p}_{AB}(\omega) \; u_{AB} \; \Delta_{AB}(c_{i+2}|c_{i+1}) \; \mathcal{B}_A(c_{i+1}|c_i) \; P_A(c_i)] \; . \qquad (2.47)$$

We now consider the second collision sequence for n=2. From (2.19) and (2.21) we obtain

$$W_2^A(\omega)_2 = \int_{-\infty}^{\infty} e^{i\omega\tau} d\tau \; \nu_A \int_0^{\infty}\int_0^{\infty} p_{AA}(x_i)\; p_{AB}(x_{i+1})$$

$$\times [<\int_{\infty}^{\infty} a_i \vec{\mu}_i(t) \cdot a_{i+2}\; \vec{\mu}_{i+2}(t-x_i-x_{i+1}+\tau)\; dt>_i$$

$$+<\int_{-\infty}^{\infty} a_i \vec{\mu}_i(t) \cdot a_{i+2}\; \vec{\mu}_{i+2}\; (t-x_i-x_{i+1}-\tau)\; dt>_i]dx_i dx_{i+1}$$

$$=2\nu_A \; \mathrm{Re}[\tilde{p}_{AA}(\omega)\; \tilde{p}_{AB}(\omega)\; <a_i \vec{\mu}_i(\omega) \cdot a_{i+2}\; \vec{\mu}_{i+2}(-\omega)>_i]$$

$$=2\nu_A \; \mathrm{Re}[\tilde{p}_{AA}(\omega)\; \tilde{p}_{AB}(\omega)\; <a_i a_{i+2}\; \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}>_i] \qquad (2.48)$$

The fraction of the coefficient $a_i a_{i+2}$ that is non-zero for this collision sequence is $u_{AA}\; u_{AB}^2$, so we have

$$W_2^A(\omega)_2 = 2\nu_A u_{AB}^2 \; \mathrm{Re}[\tilde{p}_{AA}(\omega)\; \tilde{p}_{AB}(\omega)\; u_{AA}\; <\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}>_i] \qquad (2.49)$$

From (2.38) using the given collision sequence we obtain

$$<\overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2}>_i = \int_0^{\infty} dc_{i+2} \int_0^{\infty} dc_{i+1} \int_0^{\infty} dc_i \; \mathcal{A}_A(c_{i+2})$$

$$\times \; \Delta_{AA}(c_{i+2}|c_{i+1})\; \mathcal{B}_A(c_{i+1}|c_i)\; P_A(c_i) \qquad (2.50)$$

Then we can write (2.49) as

$$W_2^A(\omega)_2 = 2\nu_A u_{AB}^2 \; \mathrm{Re}[\tilde{p}_{AB}(\omega) \int_0^{\infty} dc_{i+2} \int_0^{\infty} dc_{i+1} \int_0^{\infty} dc_i$$

$$\times \; \mathcal{A}_A(c_{i+2})\; \tilde{p}_{AA}(\omega)\; u_{AA}\Delta_{AA}(c_{i+2}|c_{i+1})\; \mathcal{B}_A(c_{i+1}|c_i) P_A(c_i)] \qquad (2.51)$$

Combining (2.47) and (2.51) we obtain for $W_2^A(\omega)$

$$W_2^A(\omega) = 2\nu_A u_{AB}^2 \operatorname{Re}[\tilde{p}_{AB}(\omega) \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times \mathcal{A}_A(c_{i+2}) \{\tilde{p}_{AB}(\omega) u_{AB} \Delta_{AB}(c_{i+2}|c_{i+1})$$

$$+ \tilde{p}_{AA}(\omega) u_{AA} \Delta_{AA}(c_{i+2}|c_{i+1})\} \mathcal{B}_A(c_{i+1}|c_i) P_A(c_i)] \qquad (2.52)$$

Letting

$$\Delta_A(c_1'|c_1) = \tilde{p}_{AB}(\omega) u_{AB} \Delta_{AB}(c_1'|c_1) + \tilde{p}_{AA}(\omega) u_{AA} \Delta_{AA}(c_1'|c_1) \qquad (2.53)$$

we have

$$W_2^A(\omega) = 2\nu_A u_{AB}^2 \operatorname{Re}[\tilde{p}_{AB}(\omega) \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times \mathcal{A}_A(c_{i+2}) \Delta_A(c_{i+2}|c_{i+1}) \mathcal{B}_A(c_{i+1}|c_i) P_A(c_i)] \qquad (2.54)$$

It can be seen in general (for arbitrary n)

$$W_n^A(\omega) = 2\nu_A u_{AB}^2 \operatorname{Re}[\tilde{p}_{AB}(\omega) \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i$$

$$\times \mathcal{A}_A(c_{i+n}) \Delta_A(c_{i+n}|c_{i+n-1}) \cdots \Delta_A(c_{i+2}|c_{i+1}) \mathcal{B}_A(c_{i+1}|c_i) P_A(c_i)] \qquad (2.55)$$

Following a collision sequence of a B molecule, one obtains a similar expression for $W_n^B(\omega)$,

$$W_n^B(\omega) = 2\nu_B u_{BA}^2 \, \mathrm{Re}[\tilde{p}_{BA}(\omega) \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i$$

$$\times \mathcal{A}_B(c_{i+n}) \Delta_B(c_{i+n}|c_{i+n-1}) \cdots \Delta_B(c_{i+2}|c_{i+1}) \; \mathcal{B}_B(c_{i+1}|c_i) P_B(c_i) \tag{2.56}$$

where

$$\Delta_B(c_1'|c_1) = \tilde{p}_{BA}(\omega) \; u_{BA} \Delta_{BA}(c_1'|c_1) + \tilde{p}_{BB}(\omega) u_{BB} \Delta_{BB}(c_1'|c_1) \tag{2.57}$$

Using the above expressions, (2.55) and (2.56), for $W_n^A(\omega)$ and $W_n^B(\omega)$ in the general expression for $W(\omega)_{\mathrm{inter}}/V$, (2.20), we obtain

$$W(\omega)_{\mathrm{inter}}/V = 2n_A \nu_A u_{AB}^2 \, \mathrm{Re}[\tilde{p}_{AB}(\omega) \sum_{n=1}^{\infty} \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i$$

$$\times \mathcal{A}_A(c_{i+n}) \Delta_A(c_{i+n}|c_{i+n-1}) \cdots \Delta_A(c_{i+2}|c_{i+1}) \; \mathcal{B}_A(c_{i+1}|c_i) P_A(c_i)]$$

$$+ 2n_B \nu_B u_{BA}^2 \, \mathrm{Re}[\tilde{p}_{BA}(\omega) \sum_{n=1}^{\infty} \int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_i$$

$$\times \mathcal{A}_B(c_{i+n}) \Delta_B(c_{i+n}|c_{i+n-1}) \cdots \Delta_B(c_{i+2}|c_{i+1}) \; \mathcal{B}_B(c_{i+1}|c_i) P_B(c_i)] \tag{2.58}$$

The quantity,

$$\int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_{i+2} \mathcal{A}_A(c_{i+n}) \Delta_A(c_{i+n}|c_{i+n-1}) \cdots \Delta_A(c_{i+2}|c_{i+1})$$

in the first term in (2.58), is the n^{th} term in the Neumann expansion of the Fredholm equation

$$G_A(\omega, c_1) = \mathcal{A}_A(c_1) + \int_0^\infty dc_1' \Delta_A(c_1'|c_1) G_A(\omega, c_1') \tag{2.59}$$

Similarly, the second term in (2.58) contains terms in the expansion of

$$G_B(\omega,c_1) = A_B(c_1) + \int_0^\infty dc_1' \Delta_B(c_1'|c_1) G_B(\omega,c_1') \qquad (2.60)$$

Since collisions far removed from an arbitrarily chosen initial collision i are only weakly correlated with it, it is likely that $W_n^A(\omega)$ and $W_n^B(\omega)$ diminish rapidly enough with increasing n for the series' in (2.20) to be convergent. Then the Neumann expansions of (2.59) and (2.60) are convergent, and the sum of the series' in (2.20) can be expressed in terms of $G_A(\omega,c_1)$ and $G_B(\omega,c_1)$. Hence we obtain

$$\begin{aligned} W(\omega)_{\text{inter}}/V &= 2n_A \nu_A u_{AB}^2 \, \text{Re}[\tilde{p}_{AB}(\omega) \int_0^\infty dc_1' \int_0^\infty dc_1 \\ &\times G_A(\omega,c_1') \, B_A(c_1'|c_1) \, P_A(c_1)] \\ &+ 2n_B \nu_B u_{BA}^2 \, \text{Re}[\tilde{p}_{BA}(\omega) \int_0^\infty dc_1' \int_0^\infty dc_1 \\ &\times G_B(\omega,c_1') \, B_B(c_1'|c_1) \, P_B(c_1)] \\ &= 2N_{AB} \int_0^\infty dc_1' \int_0^\infty dc_1 \, \text{Re}[\{\tilde{p}_{AB}(\omega) u_{AB} G_A(\omega,c_1') B_A(c_1'|c_1) P_A(c_1) \\ &+ \tilde{p}_{BA}(\omega) u_{BA} G_B(\omega,c_1') B_B(c_1'|c_1) P_B(c_1)\}] \end{aligned} \qquad (2.61)$$

We now return to our expression for the intra-collisional autocorrelation function, (2.14),

$$C(\tau)_{\text{intra}}/V = N_{AB} \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t+\tau) \rangle_i \; .$$

Then the intracollisional spectrum is given by

$$W(\omega)_{\text{intra}}/V = \int_{-\infty}^{\infty} [e^{i\omega\tau}\ C(\tau)_{\text{intra}}/V]d\tau$$

$$= N_{AB} \int_{-\infty}^{\infty} < \int_{-\infty}^{\infty} \vec{\mu}_i(t) \cdot \vec{\mu}_i(t-\tau)\ dt>_i e^{i\omega\tau} d\tau$$

$$= N_{AB} <\vec{\mu}_i(\omega) \cdot \vec{\mu}_i(-\omega)>_i \qquad (2.62)$$

Using approximation (2.26), this becomes

$$W(\omega)_{\text{intra}}/V = N_{AB} <\vec{\bar{\mu}}_i^{\,2}>_i \qquad (2.63)$$

We have

$$<\vec{\bar{\mu}}_i^{\,2}>_i = \int_0^{\infty} dc_1\ P_A(c_1) \int_0^{\infty} dc_1'\ K_A(c_1'|c_1)$$

where (2.64)

$$K_A(c_1'|c_1) = \int_0^{\pi} d\xi\ \sin\xi \int_0^{\infty} dg\ \bar{\mu}^2\ P_{AB}(g,\xi,c_1'|c_1)$$

following TIIE 2. We note that another equally valid expression for $<\vec{\bar{\mu}}_i^{\,2}>_i$ is

$$<\vec{\bar{\mu}}_i^{\,2}>_i = \int_0^{\infty} dc_1\ P_B(c_1) \int_0^{\infty} dc_1'\ K_B(c_1'|c_1)$$

where

$$K_B(c_1'|c_1) = \int_0^{\pi} d\xi\ \sin\xi \int_0^{\infty} dg\ \bar{\mu}^2\ P_{BA}(g,\xi,c_1'|c_1)$$

Now

$$W(\omega)/V = W(\omega)_{intra}/V + W(\omega)_{inter}/V$$

and using (2.61), (2.63) and (2.64) we obtain,

$$\begin{aligned} W(\omega)/V = N_{AB} \int_0^\infty dc_1' \int_0^\infty dc_1 \{ & P_A(c_1)\ K_A(c_1'|c_1) \\ & + 2\ \mathrm{Re}[\tilde{p}_{AB}(\omega)\ u_{AB} G_A(\omega,c_1')\ \mathcal{B}_A(c_1'|c_1)\ P_A(c_1) \\ & + \tilde{p}_{BA}(\omega)\ u_{BA} G_B(\omega,c_1')\ \mathcal{B}_B(c_1'|c_1)\ P_B(c_1)]\} \end{aligned} \qquad (2.65)$$

for the reduced line shape function per unit volume. We define

$$w(\omega) = W(\omega)/N_{AB}V \qquad (2.66)$$

so,

$$\begin{aligned} w(\omega) = \int_0^\infty dc_1' \int_0^\infty dc_1 \{ & P_A(c_1) K_A(c_1'|c_1) \\ & + 2\ \mathrm{Re}[\tilde{p}_{AB}(\omega)\ u_{AB} G_A(\omega,c_1')\ \mathcal{B}_A(c_1'|c_1)\ P_A(c_1) \\ & + \tilde{p}_{BA}(\omega)\ u_{BA} G_B(\omega,c_1')\ \mathcal{B}_B(c_1'|c_1)\ P_B(c_1)]\} \end{aligned} \qquad (2.67)$$

We now have an expression for the reduced line shape function for the collision-induced spectrum of an arbitrary rare-gas mixture. We have made no assumptions about the relative masses and mole fractions of the two constituents. Thus (2.67) should be generally applicable to the systems considered, within the bounds of the underlying assumptions of the theory, i.e. only binary collision contributions to the spectrum are non-negligible, the temporal superposition approximation is valid, etc.

We will now show that intercollisional interference in absorption is always destructive for the systems considered.

2.5 Intercollisional Interference at Zero Frequency

To demonstrate that intercollisional interference in absorption by binary mixtures is always destructive we require the relations

$$P_{\substack{AB\\BA}}(g,\xi,c_1',c_1) = P_{\substack{AB\\BA}}(g,\xi,c_1,c_1') \quad P(\xi,c_1',c_1) = P(\xi,c_1,c_1') \qquad (2.68)$$

where the latter relation holds for all types of collisions, AB, AA, BB, and BA collisions. These relations result from the fact that the collision $(g,\phi_g,\vec{c}_1',\vec{c}_1)$ and its inverse, $(g,-\phi_g,\vec{c}_1,\vec{c}_1')$, are equally probable, according to the Principle of Detailed Balance (TIIE 2).

Using (2.68), it is clear that

$$A_{\substack{A\\B}}(c_1'|c_1)\; P_{\substack{A\\B}}(c_1) + B_{\substack{A\\B}}(c_1|c_1')\; P_{\substack{A\\B}}(c_1') = 0 \quad , \qquad (2.69)$$

the left hand side of which can be written

$$\int_0^\pi d\xi \sin \xi \int_0^\infty dg[\overline{\mu}(g,\xi,c_1',c_1) \cos \eta(\xi,c_1',c_1) P_{\substack{AB\\BA}}(g,\xi,c_1',c_1)$$
$$+ \overline{\mu}(g,\xi,c_1,c_1') \cos \eta'(\xi,c_1,c_1') P_{\substack{AB\\BA}}(g,\xi,c_1,c_1')] \tag{2.70}$$

We have by hypothesis, $\overline{\mu}(g,\xi,c_1',c_1) = \overline{\mu}(g,\xi,c_1,c_1')$, and

$$\cos \eta(\xi,c_1',c_1) = \vec{c}_1 \cdot (\vec{c}_1{}'-\vec{c}_1)/c_1 = -\cos \eta'(\xi,c_1',c_1)$$

results from geometrical considerations. Thus (2.70) is zero.

We introduce the kernels

$$\Lambda_{\substack{A\\B}}(c_1'|c_1)_0 = P_{\substack{A\\B}}(c_1)^{\frac{1}{2}} P_{\substack{A\\B}}(c_1')^{-\frac{1}{2}} \Lambda_{\substack{A\\B}}(c_1'|c_1) \tag{2.71}$$

$$\Delta_{\substack{A\\B}}(c_1'|c_1)_0 = P_{\substack{A\\B}}(c_1)^{\frac{1}{2}} P_{\substack{A\\B}}(c_1')^{-\frac{1}{2}} \Delta_{\substack{A\\B}}(c_1'|c_1) \tag{2.72}$$

We obtain

$$B_{\substack{A\\B}}(c_1'|c_1) = -P_{\substack{A\\B}}(c_1')^{\frac{1}{2}} P_{\substack{A\\B}}(c_1)^{-\frac{1}{2}} \Lambda_{\substack{A\\B}}(c_1|c_1')_0 \tag{2.73}$$

by substituting (2.71) into (2.69). Substitution of (2.34) and (2.41), at zero frequency, into (2.72) yields

$$\Delta_{\substack{A\\B}}(c'|c)_0 = P_{\substack{A\\B}}(c)^{-\frac{1}{2}} P_{\substack{A\\B}}(c')^{-\frac{1}{2}}$$
$$\times [u_{\substack{AB\\BA}} \int_0^\pi d\xi \sin \xi \cos \xi \, P_{\substack{AB\\BA}}(\xi,c_1',c_1)$$
$$+ u_{\substack{AA\\BB}} \int_0^\pi d\xi \sin \xi \cos \xi \, P_{\substack{AA\\BB}}(\xi,c_1',c_1)] \tag{2.74}$$

Then $\Delta_{\substack{A\\B}}(c_1'|c_1)_0$ are symmetric kernels because $P(\xi,c_1',c_1)$ are symmetric in c_1 and c_1' (where $P(\xi,c_1',c_1)$ refers to the distributions for all possible types of collisions). It should be noted that $\Lambda_{\substack{A\\B}}(c_1'|c_1)_0$ is not a symmetric kernel but can be expressed in terms of two symmetric kernels (TIIE 2).

We will develop an expression for the intercollisional contribution to the spectral density at zero frequency. We define the intercollisional density as $\mathcal{D} = u_{AB}\mathcal{D}_A + u_{BA}\mathcal{D}_B$ where

$$\mathcal{D}_{\substack{A\\B}} = \int_0^\infty dc_1 \int_0^\infty dc_1' \int_0^\infty dc^{(1)} G_{\substack{A\\B}}(c_1'|c^{(1)})\ B_{\substack{A\\B}}(c^{(1)}|c_1)\ P_{\substack{A\\B}}(c_1) \tag{2.75}$$

where $G_{\substack{A\\B}}(c_1'|c_1)$ are the solutions of

$$G_{\substack{A\\B}}(c_1'|c_1) = \Lambda_{\substack{A\\B}}(c_1'|c_1) + \int_0^\infty dc_1''[u_{\substack{AB\\BA}}\ \Delta_{\substack{AB\\BA}}(c_1''|c_1)$$

$$+ u_{\substack{AA\\BB}}\ \Delta_{\substack{AA\\BB}}(c_1''|c_1)]\ G_{\substack{A\\B}}(c_1',c_1'') \tag{2.76}$$

Expanding (2.76) in Neumann series and substituting the results in (2.75), yields two infinite series, the n^{th} terms of which are

$$\left(\mathcal{D}_{\substack{A\\B}}\right)_n = \int_0^\infty dc_1 \int_0^\infty dc_1' \int_0^\infty dc^{(1)} \cdots \int_0^\infty dc^{(n+1)} A_{\substack{A\\B}}(c_1'|c^{(1)})$$

$$\times \Delta_{\substack{A\\B}}(c^{(1)}|c^{(2)})\ \Delta_{\substack{A\\B}}(c^{(2)}|c^{(3)}) \cdots \Delta_{\substack{A\\B}}(c^{(n)}|c^{(n+1)})$$

$$\times B_{\substack{A\\B}}(c^{(n+1)}|c_1)\ P_{\substack{A\\B}}(c_1) \qquad (2.77)$$

Substitution of (2.71), (2.72) and (2.73) into (2.76) gives

$$\left(\mathcal{D}_{\substack{A\\B}}\right)_n = -\int_0^\infty dc_1 \int_0^\infty dc_i' \int_0^\infty dc^{(1)} \cdots \int_0^\infty dc^{(n+1)} P_{\substack{A\\B}}(c_1')^{\frac{1}{2}} \Delta_{\substack{A\\B}}(c_1'|c_1{}^{(1)})_0$$

$$\times \Delta_{\substack{A\\B}}(c^{(1)}|c^{(2)})_0\ \Delta_{\substack{A\\B}}(c^{(2)}|c^{(3)})_0 \cdots \Delta_{\substack{A\\B}}(c^{(n)}|c^{(n+1)})_0$$

$$\times P(c_1)^{\frac{1}{2}} \Delta_{\substack{A\\B}}(c_1|c^{(n+1)})_0 \qquad (2.78)$$

Since $\Delta_{\substack{A\\B}}(c_1'|c_1)_0$ are real and symmetric, they can be expressed in terms of their orthonormalized eigenfunctions $\left(\psi_{\substack{A\\B}}\right)_m(c_i)$ even if these eigenfunctions do not form a complete set (Tricomi 1957). We then have

$$\Delta_{\substack{A\\B}}(c_1'|c_1)_0 = \sum_m \left(\epsilon_{\substack{A\\B}}\right)_m \left(\psi_{\substack{A\\B}}\right)_m (c_1') \left(\psi_{\substack{A\\B}}\right)_m (c_1) \qquad (2.79)$$

where $\left(\epsilon_{\substack{A\\B}}\right)_m$ are the real eigenvalues corresponding to $\left(\psi_{\substack{A\\B}}\right)_m$. We have used a summation sign in (2.79) although the spectrum of $\Delta_{\substack{A\\B\,0}}$ is probably partly continuous (TIIE 2).

On substituting (2.79) into (2.78) we obtain,

$$\left(\mathcal{D}_{\substack{A\\B}}\right)_n = -\sum_m \left(\varepsilon_{\substack{A\\B}}\right)_m^n \left(a_{\substack{A\\B}}\right)_m^2 \tag{2.80}$$

where the coefficients $\left(a_{\substack{A\\B}}\right)_m$ are given by

$$\left(a_{\substack{A\\B}}\right)_m = \int_0^\infty dc_1' \int_0^\infty dc_1 \; P_{\substack{A\\B}}(c_1')^{\frac{1}{2}} \; \Lambda_{\substack{A\\B}}(c_1'|c_1)_0 \left(\psi_{\substack{A\\B}}\right)_m (c_1) \tag{2.81}$$

Hence

$$\mathcal{D} = u_{AB} \sum_{n=0}^{\infty} \mathcal{D}_{A_n} + u_{BA} \sum_{n=0}^{\infty} \mathcal{D}_{B_n}$$

$$= -u_{AB} \sum_m a^2_{A_m} / (1-\varepsilon_{A_m}) - u_{BA} \sum_m a^2_{B_m} / (1-\varepsilon_{B_m}) \tag{2.82}$$

The terms $\left(\mathcal{D}_{\substack{A\\B}}\right)_n$ are the contributions of the $(n+1)^{th}$ collisions after the arbitrarily chosen initial collisions, to the intercollisional interference, for A and B terms respectively. Since later collisions are less correlated with the initial collision than earlier ones, $\left(\mathcal{D}_{\substack{A\\B}}\right)_n \to 0$ as $n \to \infty$. By (2.80), this implies that if $\left(a_{\substack{A\\B}}\right)_m$ are non-zero, then $\left|\left(\varepsilon_{\substack{A\\B}}\right)_m\right| < 1$.

Hence $\left(a_{\substack{A\\B}}\right)_m^2/(1-\left(\varepsilon_{\substack{A\\B}}\right)_m)>0$ for all m, and then, from (2.82), $\mathcal{D}\leq 0$. In other words, at zero frequency, the intercollisional contribution to the spectral density is always negative.

However, unlike TIIE 2, the extension of the property to non-zero frequencies is not easy. This is because the quantities $\Delta_{\substack{A\\B}}(c_1'|c_1)$ are frequency dependent, and this dependence cannot be split out as a multiplying factor in the Neumann expansions of the Fredholm equations (2.76).

We recall the general equation for the line shape function of the collision-induced absorption spectrum, $w(\omega)$, (2.67). To evaluate the quantities in (2.67) involving collision probability distributions is difficult, even for simple physical models (TIIE 2). The calculations of $P_{AB}(\xi,\vec{c}_1'|\vec{c}_1)$ and $\Delta_{AB}(\vec{c}_1'|\vec{c}_1)$ for a rigid-sphere gas are performed in section 4 of TIIE 2. Because of the difficult evaluation of collision probability distributions, we will not attempt to use our expression in its general form in the study of $w(\omega)$. Instead, we look for a simplification that will reduce (2.67) to a form where the dependence of $w(\omega)$ on mole fraction can be more easily obtained.

2.6 A Simplified Expression for the Line-Shape Function

A simplified expression for the line shape function can be obtained by approximating $\Delta(c_1'|c_1)$ by the mean persistence-of-velocity ratio, as was first considered in TIIE 2. Consider the Fredholm equations

$$G_{\substack{A\\B}}(\omega,c_1) = A_{\substack{A\\B}}(c_1) + \int_0^\infty dc_1' \, \Delta_{\substack{A\\B}}(c_1'|c_1) \, G_{\substack{A\\B}}(\omega,c_1), \qquad (2.83)$$

the solutions of which occur in (2.67). To obtain the solutions to these equations, where $\Delta_{\substack{A\\B}}(c_1'|c_1)$ have general velocity dependences, we use a Neumann expansion of each of the two terms and obtain a pair of infinite series. However, if the functional dependence of $\Delta_{\substack{A\\B}}(c_1'|c_1)$ on velocity is replaced by some average value, $\tilde{\Delta}_{\substack{A\\B}}$;

$$\Delta_{\substack{A\\B}}(c_1'|c_1) = \tilde{\Delta}_{\substack{A\\B}} \, \delta(c_1'-c_1) \qquad (2.84)$$

where δ is the Dirac delta function, the solutions to the Fredholm equations (2.83) can be readily expressed in closed form,

$$G_{\substack{A\\B}}(\omega,c_1) = A_{\substack{A\\B}}(c_1)/(1-\tilde{\Delta}_{\substack{A\\B}}(\omega)) \qquad (2.85)$$

where

$$\tilde{\Delta}_{\substack{A\\B}}(\omega) = \tilde{p}_{\substack{AB\\BA}}(\omega) \, u_{\substack{AB\\BA}} \, \tilde{\Delta}_{\substack{AB\\BA}} + \tilde{p}_{\substack{AA\\BB}}(\omega) \, u_{\substack{AA\\BB}} \, \tilde{\Delta}_{\substack{AA\\BB}} \qquad (2.86)$$

The quantities $\tilde{\Delta}_{\substack{AB\\BA}}$ and $\tilde{\Delta}_{\substack{AA\\BB}}$ in (2.86) are of course the averages occuring in relations similar to (2.84);

$$\Delta(c_1'|c_1) \approx \tilde{\Delta}\ \delta(c_1'-c_1) \quad , \qquad (2.87)$$

where (2.87) refers to all possible types of collisions; AB, AA; BB, and BA collisions.

If we are dealing with a rigid sphere Lorentz gas ($n_A << n_B$, $m_A << m_B$), (2.87) for AB collisions, is exact if $\tilde{\Delta}_{AB}$ is taken as speed dependent (TIIE 2). In addition, this relation is also valid if $m_A >> m_B$ (TIIE 2). Thus it appears likely that (2.87) for AB collisions, is valid for arbitrary values of m_A/m_B. Given this, it is reasonable to assume that (2.87) is a good approximation for all types of collisions, AB, AA, BB, and BA collisions, for arbitrary mass ratios.

The quantities $\tilde{\Delta}$ in (2.87) are some average value of $\Delta(c_1'|c_1)$, and are a measure of the persistence of the velocity of a molecule in a collision ($\tilde{\Delta}_{\substack{AB\\BA}}$ is a measure of persistence of the velocity of a molecule $\substack{A\\B}$ in a collision with a $\substack{B\\A}$ molecule, similarly for $\tilde{\Delta}_{\substack{AA\\BB}}$). If we choose our mean value of $\Delta_{AB}(c_1'|c_1)$ to be

$$\tilde{\Delta}_{AB} = \int_0^\infty dc_1' \int_0^\infty dc_1\, (c_1'/c_1)\ \Delta_{AB}(c_1'|c_1)\ P_A(c_1) \quad , \qquad (2.88)$$

we find that $\tilde{\Delta}_{AB}$ is identical to the mean persistence-of-velocity ratio ω_{AB} defined for rigid spheres by Chapman and Cowling (1964). They have derived this ratio for rigid spheres with arbitrary values of m_A/m_B and obtained

$$\tilde{\Delta}_{AB} = M_A/2 + (M_A^2/2M_B^{\frac{1}{2}}) \ln[(M_B^{\frac{1}{2}} + 1)/M_A^{\frac{1}{2}}] \qquad (2.89)$$

where $M_A = m_A/m_0$ and $M_B = m_B/m_0$ with $m_0 = m_A + m_B$. From this expression we can see that $\tilde{\Delta}_{AB}$ is solely dependent on the relative masses of the two species, and that it varies from 0 for $\frac{M_A}{M_B} \rightarrow 0$, to 1 for $\frac{M_A}{M_B} \rightarrow \infty$, and is approximately 0.406 for $M_A = M_B$.

If $\tilde{\Delta}_{AA}$, $\tilde{\Delta}_{BB}$ and $\tilde{\Delta}_{BA}$ are defined in expressions similar to that of $\tilde{\Delta}_{AB}$, that is (2.88), we find that these mean values are identical to corresponding mean persistence-of-velocity ratio. These ratios are defined of course in relations similar to (2.89):

$$\tilde{\Delta}_{IJ} = M_I/2 + (M_I^2/2M_J^{\frac{1}{2}}) \ln[(M_J^{\frac{1}{2}} + 1)/M_I^{\frac{1}{2}}] \qquad (2.90)$$

where I = A or B, and J = A or B. Clearly $\tilde{\Delta}_{AA}$ and $\tilde{\Delta}_{BB}$ are independent of the mass ratio, and have a common value of approximately 0.406.

We return to the solutions of the Fredholm equations, (2.85), obtained by using the simplification (2.84),

$$G_{\substack{A\\B}}(\omega,c_1) = \mathcal{A}_{\substack{A\\B}}(c_1)/(1 - \tilde{\Delta}_{\substack{A\\B}}(\omega)).$$

Substituting these solutions into our general expression for the line shape function, (2.67), we obtain

$$w(\omega) = \mathcal{C} + 2\,\mathrm{Re}[u_{AB}\,\tilde{p}_{AB}(\omega)\;\alpha_A/(1 - \tilde{\Delta}_A(\omega))$$

$$+ u_{BA}\,\tilde{p}_{BA}(\omega)\;\alpha_B/(1 - \tilde{\Delta}_B(\omega))] \tag{2.91}$$

where we have used the following definitions;

$$\mathcal{C} = \int_0^\infty dc_1\;P_A(c_1)\int_0^\infty dc_1'\;K_A(c_1'|c_1) \tag{2.92}$$

and

$$\alpha_{\substack{A\\B}} = \int_0^\infty dc_1\;P_{\substack{A\\B}}(c_1)\int_0^\infty dc_1'\;\mathcal{A}_{\substack{A\\B}}(c_1')\;B_{\substack{A\\B}}(c_1'|c_1)\;. \tag{2.93}$$

$\mathcal{C}$ is the intracollisional part of the spectrum, and α_A and α_B are due to intercollisional interference.

At zero frequency we have

$$w(0) = \mathcal{C} + 2\;u_{AB}\;\alpha_A/(1 - \tilde{\Delta}_A(0))$$

$$+ 2\;u_{BA}\;\alpha_B/(1 - \tilde{\Delta}_B(0)) \tag{2.94}$$

where

$$\tilde{\Delta}_{\substack{A\\B}}(0) = u_{\substack{AB\\BA}}\,\tilde{\Delta}_{\substack{AB\\BA}} + u_{\substack{AA\\BB}}\,\tilde{\Delta}_{\substack{AA\\BB}} \tag{2.95}$$

We now introduce the quantities $z = n_A/n_B$ and $r_{\substack{A\\B}} = S_{\substack{A\\B}}/S_{AB}$ and write the relative collision frequencies in terms of these variables to obtain

$$u_{AA} = r_A\, z/(1 + r_A z)\ ;\ u_{AB} = 1/(1 + r_A z)$$

$$u_{BB} = (1/z)/(1 + r_B/z)\ ;\ u_{BA} = 1/(1 + r_B/z)\ . \tag{2.96}$$

The limiting cases (1) $z \to 0$ and (2) $z \to \infty$ are now considered. In the first case, the relative collision frequencies, to the first order in z, are

$$u_{AA} \sim \mathcal{O}(z),\ u_{BA} \sim \mathcal{O}(z),\ u_{AB} \sim 1-\mathcal{O}(z),\ u_{BB} \sim 1-\mathcal{O}(z). \tag{2.97}$$

In the second case, the relative collision frequencies, to the first order in 1/z, are

$$u_{AA} \sim 1-\mathcal{O}(1/z),\ u_{BA} \sim 1-\mathcal{O}(1/z),\ u_{AB} \sim \mathcal{O}(1/z),\ u_{BB} \sim \mathcal{O}(1/z). \tag{2.98}$$

We consider limiting case (1) first. Substituting (2.97) into (2.94), we obtain

$$w(0) \sim C + 2[1-O(z)]\,\alpha_A/\{1-[1-O(z)]\tilde{\Delta}_{AB} - [O(z)]\,\tilde{\Delta}_{AA}\} + 2[O(z)]\,\alpha_B/\{1-[O(z)]\,\tilde{\Delta}_{BA} - [1-O(z)]\,\tilde{\Delta}_{BB}\} \qquad (2.99)$$

for the line shape function at zero frequency, to the first order in z. Considering only the terms of order unity, we obtain

$$w(0) \sim C + 2\,\alpha_A/(1-\tilde{\Delta}_{AB}). \qquad (2.100)$$

The depth of the intercollisional dip relative to the intracollisional spectrum is usually written as 1-γ (Van Kranendonk 1968). Thus, for the first limiting case, we have

$$w(0) \equiv C(1-\gamma_A) = C + 2\alpha_A/(1-\tilde{\Delta}_{AB})$$

yielding

$$2\alpha_A = -C(1-\tilde{\Delta}_{AB})\gamma_A. \qquad (2.101)$$

Similarly in the second limiting case we obtain

$$2\alpha_B = -C(1-\tilde{\Delta}_{BA})\gamma_B. \qquad (2.102)$$

Substituting (2.101) and (2.102) into (2.91) yields

$$w(\omega) = C\{1-u_{AB}(1-\tilde{\Delta}_{AB})\ \gamma_A\ \mathrm{Re}[\tilde{p}_{AB}(\omega)/(1-\tilde{\Delta}_A(\omega))]$$

$$-u_{BA}(1-\tilde{\Delta}_{BA})\ \gamma_B\ \mathrm{Re}[\tilde{p}_{BA}(\omega)/(1-\tilde{\Delta}_B(\omega))]\} \qquad (2.103)$$

which is our simplified expression for the line shape function.

2.7 Calculations and Results

The dependence of the relative line shape function on frequency and mole fraction can now be easily obtained using (2.103). In particular, we wish to study the variation of the halfwidth of the line shape function with the mole fraction of one of the constituents. This dependence cannot be readily calculated analytically and we resort to computer calculations based on the Newton-Raphson algorithm. The basic procedures followed in these calculations will now be outlined along with the principal results.

Since it is primarily our aim to study dependence on mole fraction, we find it convenient to treat those terms independent of number density as constants. We set the intercollisional term C equal to unity, so that if there are no intercollisional effects present, $w(\omega)=1$. Likewise, it is reasonable to assign the quantities γ_A and γ_B value 1. Our expression for the line shape function is now reduced to

$$w(\omega) = 1 - u_{AB}(1-\tilde{\Delta}_{AB})\mathrm{Re}[\tilde{p}_{AB}(\omega)/(1-\tilde{\Delta}_A(\omega))]$$

$$- u_{BA}(1 - \tilde{\Delta}_{BA})\ \mathrm{Re}[\tilde{p}_{BA}(\omega)/(1-\tilde{\Delta}_{B}(\omega))]. \tag{2.104}$$

We recall that $\tilde{p}_{\substack{AB\\BA}}(\omega)$ are related to the probability distributions for collision intervals x_i for $\substack{AB\\BA}$ collisions, $p_{\substack{AB\\BA}}(x_i)$, by

$$\tilde{p}_{\substack{AB\\BA}}(\omega) = \int_0^\infty e^{-i\omega x_i}\, p_{\substack{AB\\BA}}(x_i)\, dx_i .$$

Following TIIE 2, we assume that the intervals x_i are independently distributed as

$$p_{\substack{AB\\BA}}(x_i) = \nu_{\substack{AB\\BA}}\, e^{-\nu_{\substack{AB\\BA}} x_i} \tag{2.105}$$

where $\nu_{\substack{AB\\BA}}$ are the average collision frequencies for $\substack{AB\\BA}$ collisions. We have of course, similar expressions for $p_{\substack{AA\\BB}}(x_i)$ that appear in $\tilde{\Delta}_A(\omega)$ and $\tilde{\Delta}_B(\omega)$, through $\tilde{p}_{\substack{AA\\BB}}(\omega)$. Equation (2.105) is valid if the collision frequencies are velocity-independent and the assumption of molecular chaos holds (TIIE 2). The use of this approximation is discussed in detail in TIIE 2, where it is pointed out that (2.105) is unlikely to introduce significant errors.

Substituting (2.105) into our expression for $\tilde{p}_{\substack{AB\\BA}}(\omega)$, we obtain

$$\tilde{p}_{\substack{AB\\BA}}(\omega) = \nu_{\substack{AB\\BA}}/(\nu_{\substack{AB\\BA}} + i\omega) \tag{2.106}$$

where $\nu_{\substack{AB\\BA}} = N_{AB}/n_{\substack{A\\B}}$, with a similar expression for $\tilde{p}_{\substack{AA\\BB}}(\omega)$. We now have all of the variables appearing in (2.104) in terms of the defining parameters of rigid-sphere molecules, that is, rigid-sphere diameter σ, and mass m.

We will write (2.104) in terms of the collision probabilities u, mean persistance-of-velocities $\tilde{\Delta}$, average collisional frequencies ν, and collision frequencies per unit volume N, where these quantities will be denoted with the appropriate subscripts. The definitions of these variables in terms of σ and m are then given, and values assigned to these parameters and the constants characterizing the gas mixtures.

$$w(\omega) = 1 - u_{AB}(1-\tilde{\Delta}_{AB})\ \mathrm{Re}\{[\nu_{AB}/(\nu_{AB} + i\omega)]$$

$$\times\ [1-[\nu_{AB}/(\nu_{AB} + i\omega)]u_{AB}\tilde{\Delta}_{AB}-[\nu_{AA}/(\nu_{AA} + i\omega)]u_{AA}\tilde{\Delta}_{AA}]^{-1}\}$$

$$-\ u_{BA}(1-\tilde{\Delta}_{BA})\ \mathrm{Re}\{[\nu_{BA}/(\nu_{BA}+i\omega)]$$

$$\times\ [1-[\nu_{BA}/(\nu_{BA}+i\omega)]u_{BA}\tilde{\Delta}_{BA}-[\nu_{BB}/(\nu_{BB}+i\omega)]u_{BB}\tilde{\Delta}_{BB}]^{-1}\} \quad (2.107)$$

where

$$u_{\substack{AB\\BA}} = N_{\substack{AB\\BA}}/(N_{\substack{AA\\BB}} + N_{\substack{AB\\BA}}),$$

$$u_{\substack{AA\\BB}} = N_{\substack{AA\\BB}}/(N_{\substack{AA\\BB}} + N_{\substack{AB\\BA}}),$$

$$\nu_{\substack{AB\\BA}} = N_{\substack{AB\\BA}}/n_{\substack{A\\B}} \quad \nu_{\substack{AA\\BB}} = N_{\substack{AA\\BB}}/n_{\substack{A\\B}} \quad ,$$

$$\tilde{\Delta}_{\substack{AB\\BA}} = M_{\substack{A\\B}}/2 + (M^2_{\substack{A\\B}}/2\ M^{\frac{1}{2}}_{\substack{B\\A}})\ \ln[(M^{\frac{1}{2}}_{\substack{B\\A}} + 1)/M^{\frac{1}{2}}_{\substack{A\\B}}],$$

$$\tilde{\Delta}_{\substack{AA\\BB}} = 0.406\ ,$$

and

$$N_{\substack{AB\\BA}} = n_A n_B S_{AB}$$

$$N_{\substack{AA\\BB}} = n^2_{\substack{A\\B}}\ S_{\substack{A\\B}}\ ,$$

with

$$S_{AB} = 2\ \pi\sigma^2_{AB}\sqrt{2kTm_o/\pi m_A m_B}$$

and

$$S_{\substack{A\\B}} = 4\ \pi\sigma^2_{\substack{A\\B}}\sqrt{kT/\pi m_{\substack{A\\B}}}\ ,$$

where $m_o = m_A + m_B$ and we have used $\Sigma_{AB} = \pi\sigma_{AB}^2 = \pi(\sigma_A+\sigma_B)^2/4$, and $\Sigma_{AA} = \pi\sigma_A^2$.

$k \equiv$ Boltzmann's constant $= 1.38 \times 10^{-16}$ ergs/degree.

$T \equiv$ room temperature $= 300$ K.

We will study the line shapes for six different mixtures; He-Ne, He-Ar, He-Xe, Ne-Ar, Ar-Xe, and Ne-Xe. The numerical values of various parameters are given below.

TABLE 2.1. Values of the Rigid-Sphere Parameters for He, Ne, Ar, and Xe.

molecule	σ_A* (Å)	Σ_{AA} (Å^2)	m_A (amu)	S_A (Å^{2}cm/sec)
He	1.80	10.2	4.003	1.82×10^6
Ne	2.80	24.6	20.183	1.95×10^6
Ar	3.40	36.3	39.944	2.05×10^6
Xe	4.00	50.3	131.30	1.56×10^6

*The values of σ_A are taken from Hirschfelder, Curtiss and Bird, (1967), and Chapman and Cowling (1970).

TABLE 2.2. Values of the Rigid-Sphere Parameters for He-Ne, He-Ar, He-Xe, Ne-Ar, Ar-Xe, and Ne-Xe Mixtures.

mixture A-B	σ_{AB} (Å)	Σ_{AB} (Å^2)	S_{AB} (Å^{2}cm/sec)	$\tilde{\Delta}_{AB}$	$\tilde{\Delta}_{BA}$
He-Ne	2.30	16.6	2.29×10^6	.106	.787
He-Ar	2.60	21.2	2.80×10^6	.054	.881
He-Xe	2.90	26.4	3.38×10^6	.016	.961
Ne-Ar	3.10	30.2	2.08×10^6	.247	.584
Ar-Xe	3.70	40.3	1.96×10^6	.159	.704
Ne-Xe	3.40	36.3	2.19×10^6	.082	.827

A typical plot of the line shape as a function of frequency produced from (2.107) is shown in Figure 2.5. This plot was obtained for the He-Ne mixture at a density of 100 amagat, and mole fraction of He, x_A, equal to 0.1. It should be noted that the line shape function is not a Lorentzian. In particular, there is a small feature, about 1% of the intracollisional spectrum at zero frequency, appearing at about 0.5 cm^{-1}. This structure, however, arises when absorption is very high and is not likely to be observed experimentally. If we plot the line shape as a function of frequency for the He-Ne mixture with the same density but for mole fraction, x_A, equal to 0.01, we obtain a Lorentzian -like curve with a

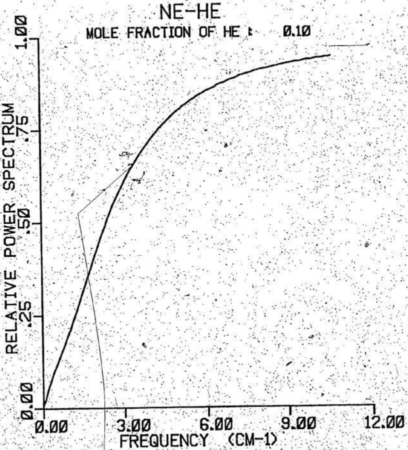

FIGURE 2.5. Relative Power Spectrum w(ω) of the He-Ne Mixture for a Mole Fraction of He = 0.1 and Density = 100 Am.

halfwidth of $\nu_{AB}(1-\tilde{\Delta}_{AB})$ in agreement with the TIIE 2 result for infinite dilution (see Figure 2.6).

To study how the line shape varies with relative number density, it is useful to obtain the dependence of the halfwidth on the mole fraction of one of the constituents. The halfwidth, $\omega_{\frac{1}{2}}$, at a given mole fraction is the frequency for which the line shape has value $(W(\omega)_{max} - W(\omega)_{min})/2$, or $(1-W(0))/2$. This halfwidth is obtained using a simple iterative Newton-Raphson procedure, the outline of which is given below.

Initially, the trial halfwidth (usually obtained from a plot of $W(\omega)$ vs ω at the given mole fraction), and the frequency interval for which the derivative of the line shape is to be calculated, which we denote by ω_{trial} and Δ_{ω} respectively, are input. The frequency interval Δ_{ω} being typically of the order of $\omega_{trial}/100$. A brief description of the major calculations in the program are as follows:

1) The value of the line shape function for the given mole fraction at $\omega = \omega_{\frac{1}{2}}$, $W(\omega_{\frac{1}{2}}) = (1-W(0))/2$ is computed.

2) The difference between $W(\omega_{trial})$ and $W(\omega_{\frac{1}{2}})$ is calculated and we denote it by ΔW.

3) If $\Delta W < 0.0001$, ω_{trial} is assigned as the halfwidth $\omega_{\frac{1}{2}}$.

4) If $\Delta W > 0.0001$, a new trial halfwidth is defined

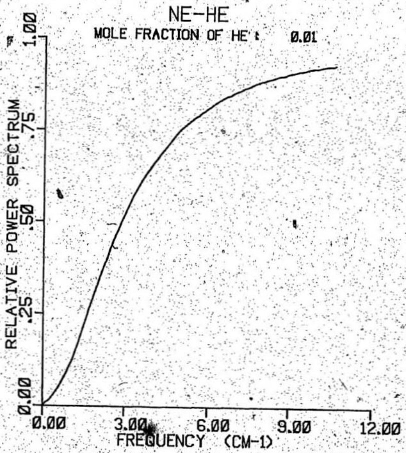

FIGURE 2.6. Relative Power Spectrum w(ω) of the He-Ne Mixture for a Mole Fraction of He = 0.01 and Density = 100 Am.

by

$$\omega^{(1)}_{\text{trial}} = \omega_{\text{trial}} + \Delta\omega/W'$$

where

$$W' = [W(\omega_{\text{trial}} + \Delta\omega) - W(\omega_{\text{trial}})]/\Delta\omega.$$

5) return to step (2).

This process is repeated until condition (3) is satisfied or until the number of iterations exceeds 20. To obtain the dependence of $\omega_{\frac{1}{2}}$ on mole fraction, steps (1) to (5) are executed inside an iterative loop for the mole fraction of the lighter molecule, denoted x_A, where x_A is incremented by step sizes Δx_A from 0 to 1. The increment Δx_A is input along with the density of the mixture at the start of the program. The value of the trial halfwidth for each value of the mole fraction is assigned the value of previously calculated $\omega_{\frac{1}{2}}$. As can be seen from Figure 2.5 and 2.6, $W(\omega)$ is a well behaved function, and the number of iterations required to obtain a suitable $\omega_{\frac{1}{2}}$ is typically small, usually 2 or 3.

The plots obtained by the above program are shown in Figures 2.7 to 2.10, for He-Ne, He-Ar, He-Xe and Ne-Ar mixtures respectively. The values of the halfwidths for $x_A \to 0$ and $x_A \to 1$ are in agreement with the result $\omega_{\frac{1}{2}} = \nu_{\substack{AB\\BA}}(1-\Delta_{\substack{AB\\BA}})$ obtained in TIIE.2 for infinite dilution. The density is

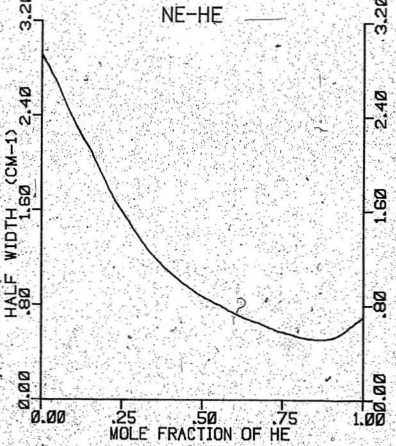

FIGURE 2.7. Halfwidth of the Intercollisional Spectrum versus Mole Fraction of He for the He-Ne Mixture.

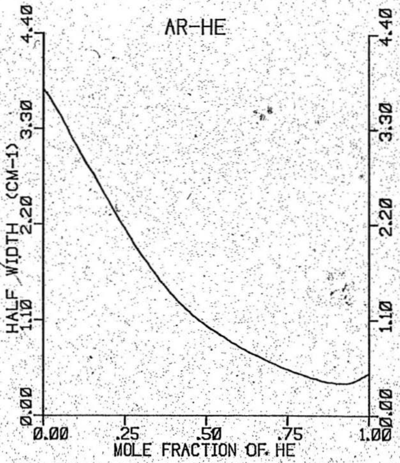

FIGURE 2.8. Halfwidth of the Intercollisional Spectrum versus Mole Fraction of He for the He-Ar Mixture.

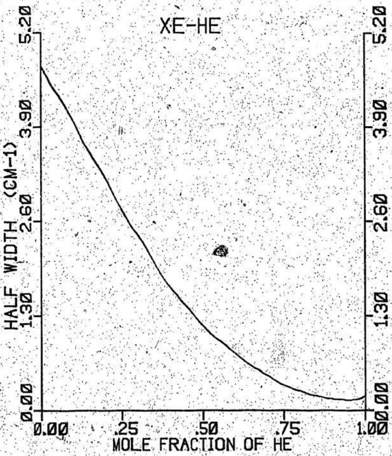

FIGURE 2.9. Halfwidth of the Intercollisional Spectrum versus Mole Fraction of He for the He-Xe Mixture.

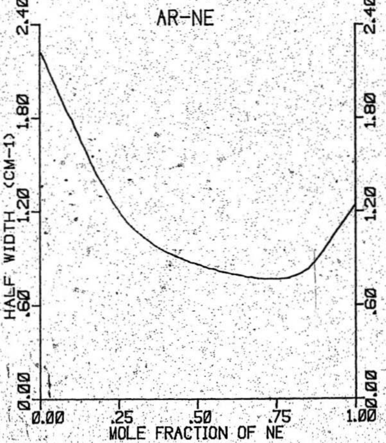

FIGURE 2.10. Halfwidth of the Intercollisional Spectrum versus Mole Fraction of Ne for the Ne-Ar Mixture.

100 amagat for all of the plots shown.

One of the major features of the plots is that the halfwidth does not go to its minimum value as x_A goes to 1. This is particularly obvious for the He-Ne mixture and especially so for the Ne-Ar mixture. We note that the latter mixture is differentiated from the other mixtures mainly in that the masses of the two constituents are fairly close. The location of this minimum halfwidth was unexpected.

Let us consider a binary gas mixture with constituents A and B. As before, A denotes the less massive of the two species, thus $\tilde{\Delta}_{AB}<\tilde{\Delta}_{BA}$. Assume x_A is very close to 1, and the gas can be treated as a single B molecule in a sea of light A molecules. We now increase the concentration of B molecules, and/or decrease that of A, until the gas can be treated as a single A molecule moving in a sea of heavier B molecules. Initially it was thought that the halfwidth would increase from its value at $x_A \approx 1$, $nS_{AB}(1-\tilde{\Delta}_{BA})$ to its value at $x_A \approx 0$, $nS_{AB}(1-\tilde{\Delta}_{AB})$. This is not the case as can be seen from Figures 2.7 to 2.10. The reason why the interference is maximal at $x_A \approx 0$ is obvious. Any increase in the concentration of A molecules will result in AA collisions which tend to spoil the negative correlation in the dipole-inducing collisions, that is AB collisions. Correspondingly, it seemed likely that for $x_A \approx 1$, the interference would be minimal. However, upon closer examination of the behaviour of the halfwidth for $x_A \approx 1$, the effect of an increase in the concentration of B molecules is not immediately obvious.

2.8 Comparison with Experiment; Conclusions

Wong (1978) has obtained an expression for the line shape function of absorption by arbitrary binary rare-gas mixtures. In our notation, his result, (6.4.2), can be expressed as

$$W(\omega) = C + \frac{2u_{AB}\alpha_A}{1+(\omega/\nu_{AB})^2} + \frac{2u_{BA}\alpha_B}{1+(\omega/\nu_{BA})^2} .$$

In the above expression, the quantities α_A and α_B are treated as adjustable parameters. The values assigned to these quantities are obtained by a curve-fitting procedure. This was done for Ne-Xe and Ar-Xe mixtures for various concentration ratios at 2.3 cm^{-1} and 4.5 cm^{-1}. Not unexpectedly, the agreement between these fitted curves and the experimental data is good (see Figures 2.11-2.13). However, at lower frequencies these fitted parameters yield negative values for the line shape function and thus cannot be regarded as physically realistic or meaningful.

As mentioned previously in section 2.6, $1-\gamma_A \sim 1-\gamma_B \sim 0$, and as a result the quantities α_A/C and α_B/C can be calculated (see (2.101) and (2.102)). We obtain

$$\alpha_{\substack{A\\B}}/C = -(1-\tilde{\Delta}_{\substack{AB\\BA}})/2 . \qquad (2.108)$$

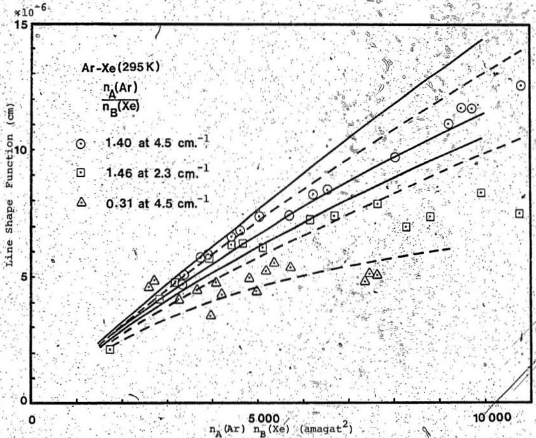

FIGURE 2.11 Intercollisional line shapes for the Ar-Xe mixture at 2.3 cm^{-1} and 4.5 cm^{-1}. (Solid lines represent our curves, dashed lines represent fitted curves.) Experimental data is from Wong (1978).

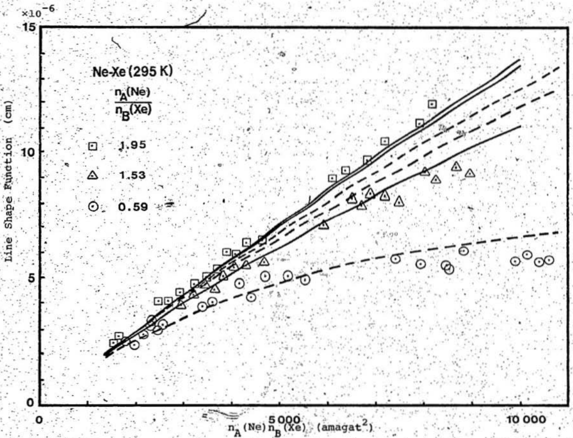

FIGURE 2.12 Intercollisional line shapes for the Ne-Xe mixture at 4.5 cm^{-1}. (Solid lines represent our curves, dashed lines represent fitted curves.) Experimental data is from Wong (1978).

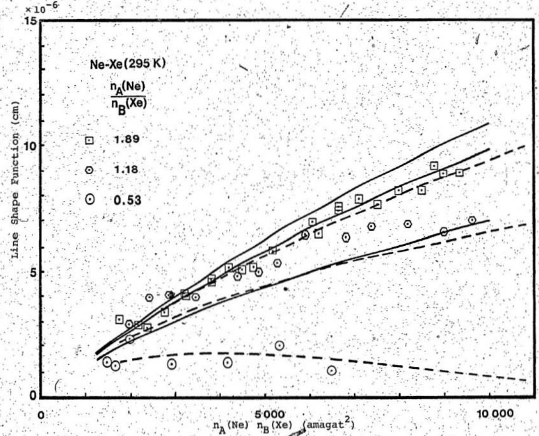

FIGURE 2.13 Intercollisional line shapes for the Ne-Xe mixture at 2.3 cm^{-1}. (Solid lines represent our curves, dashed lines represent fitted curves.) Experimental data is from Wong (1978).

For any realistic three-dimensional system $\tilde{\Delta}_{\substack{AB\\BA}}$ are non-negative and so

$$|\alpha_{\substack{A\\B}}/C| \le \tfrac{1}{2} \tag{2.109}$$

In the following table, we present our values of $\alpha_{\substack{A\\B}}/C$ calculated with (2.108) and those of Wong.

Table 2.3. Analytical and Fitted Values of $\alpha_{\substack{A\\B}}/C$ for Ne-Xe and Ar-Xe.

	Ne-Xe		Ar-Xe	
	α_A/C	α_B/C	α_A/C	α_B/C
Present Work	-.45	-.08	-.42	-.15
Wong	-.850	-.025	-.675	-.115

The values bear only a qualitative similarity. It is clear that Wong's values for α_A/C violate the inequality (2.109) necessary for the non-negativity of the line shape function.

The curves calculated by our expression for intercollisional line shape, (2.103), are shown in Figures 2.11 to 2.13. These curves were generated by using line shape values computed by the program described in section 2.7, multiplied by the value of the intracollisional spectrum at low frequency, obtained by Wong and multiplied by the factor $n_A n_B$. It should be noted that the differences in the fitted curves and ours are not due to differences in the values of physical parameters, i.e. the intracollisional term or rigid-sphere diameters, but rather to the different form of the intercollisional line shape function.

We conclude that our theory gives the correct qualitative behaviour of the intercollisional dip. This is demonstrated in Figures 2.11 to 2.13, where up to 5,000 Am^2 our curves generally fit the experimental data as well as the fitted curves. However, it is clear that the correlations that we have neglected, i.e. the fourth term in (2.6), are significant. They give rise to the serious differences between the theory and experiment, particularly at higher densities. In addition, w(0) is markedly greater than zero for $0<x_A<1$ even when our theory forces $w(0) = 0$ for $x_A = 0$ and $x_A=1$. This is also a problem in collision-induced light scattering, but is not so prevalent since the correlations are weaker. The contribution to the total intercollisional interference from immediately successive collisions is about 65% for light scattering (TIIE 3).

The approach of TIIE 1-5 and the present work requires further elaboration to account for the above correlations. Extensions of the applicability of the theory to higher densities requires the inclusion of ternary and higher-order collision processes.

In the following chapter we shall extend the theory developed above to mixtures, not merely of arbitrary concentration ratio but of arbitrary numbers of components.

CHAPTER 3

THEORY OF INTERCOLLISIONAL INTERFERENCE IN TRANSLATIONAL ABSORPTION BY GAS MIXTURES OF ARBITRARY COMPOSITION

3.1 Introduction

This chapter deals with intercollisional interference in absorption by gas mixtures consisting of an arbitrary number of species. We make no assumptions about the relative masses and number densities of the species. However, as in Chapter 2 the assumption that $\tau_c >> \tau_d$ will be made so that only low densities will be considered. A temporal superposition for the dipole moments induced in isolated binary collisions can then be used to represent the induced dipole moment in a particular molecule. In addition, we assume that unlike molecules interact through pairwise additive central forces, and that the induced dipole moments are pairwise additive and instantaneously parallel to these forces, as in Chapter 2. Our treatment begins again with the expression for the total induced dipole moment in the gas at time t.

3.2 General Theory

Consider a gas in a volume V, consisting of species $\alpha, \beta, \ldots, \omega$ with the numbers of molecules of each species denoted by $N_\alpha, N_\beta, \ldots, N_\omega$ respectively. A molecule of species γ will be denoted a_γ. The total induced dipole moment in the gas can be written

$$\vec{M}(t) = \tfrac{1}{2}\{\sum_{a_\alpha=1}^{N_\alpha}\sum_{b=1}^{N-N_\alpha}\vec{\mu}^{(a_\alpha b)}(t) + \sum_{a_\beta=1}^{N_\beta}\sum_{b}^{N-N_\beta}\vec{\mu}^{(a_\beta b)}(t) + \ldots$$

$$\ldots + \sum_{a_\omega=1}^{N_\omega}\sum_{b}^{N-N_\omega}\vec{\mu}^{(a_\omega b)}(t) \qquad (3.1)$$

where $\vec{\mu}^{(a_\varepsilon b)}(t)$ is the dipole moment induced by the intermolecular interaction between molecules a_ε and b. Since molecules of the same species do not induce dipoles in each other, i.e.

$$\vec{\mu}^{(a_\varepsilon a_\varepsilon')}(t) = 0 ;$$

we can write the total induced dipole moment as

$$\vec{M}(t) = \tfrac{1}{2}\sum_{b=1}^{N}\{\sum_{a_\alpha=1}^{N_\alpha}\vec{\mu}^{(a_\alpha b)}(t) + \ldots + \sum_{a_\omega=1}^{N_\omega}\vec{\mu}^{(a_\omega b)}(t)\}$$

$$= \tfrac{1}{2}\sum_{\varepsilon=\alpha}^{\omega}\sum_{b}\sum_{a_\varepsilon}\vec{\mu}^{(a_\varepsilon b)}(t)$$

$$= \tfrac{1}{2}\sum_{a}\sum_{b}\vec{\mu}^{(ab)}(t) \quad . \qquad (3.2)$$

This expression corresponds to (2.4) but is written in a different form so that summation extends over all the molecules in the gas. From our expression for the dipole moment autocorrelation function, (2.3), we have

$$C(\tau) = \tfrac{1}{4} < \sum_{a,a'} \sum_{b,b'} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b')}(t+\tau)> \qquad (3.3)$$

This expression will be handled in the same manner as (2.5). That is, we can write (3.3) as

$$\tfrac{1}{4} <2 \sum_{a} \sum_{b,b'} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab')}(t+\tau)$$

$$+ 2 \sum_{b} \sum_{a,a'} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b)}(t+\tau)$$

$$- 2 \sum_{a} \sum_{b} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t+\tau)$$

$$+ \sum_{\substack{a,a' \\ a \neq a',b'}} \sum_{\substack{b,b' \\ b \neq b',a'}} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(a'b')}(t+\tau)> \qquad (3.4)$$

where we have used the fact that

$$\vec{\mu}^{(a_\varepsilon b_\gamma)}(t) = \vec{\mu}^{(b_\gamma a_\varepsilon)}(t) \quad . \qquad (3.5)$$

Again, as in Chapter 2, the last term which expresses correlations between collisions in which no molecule is common, will be neglected. Let the dipole moment induced by a molecule a_γ of species γ in all other molecules by

$$\vec{\mu}^{(a_\gamma)}(t) = \sum_{b} \vec{\mu}^{(a_\gamma b)}(t) \quad . \qquad (3.6)$$

Writing (3.4) as

$$C(\tau) = \frac{1}{2} < \sum_{\varepsilon} \sum_{a_\varepsilon} \sum_{b,b'} \vec{\mu}^{(a_\varepsilon b)}(t) \cdot \vec{\mu}^{(a_\varepsilon b')}(t + \tau)$$

$$+ \sum_{\varepsilon} \sum_{b_\varepsilon} \sum_{a,a'} \vec{\mu}^{(a b_\varepsilon)}(t) \cdot \vec{\mu}^{(a' b_\varepsilon)}(t + \tau)$$

$$- \sum_{a} \sum_{b} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t + \tau)> \qquad (3.7)$$

and using (3.6) we obtain

$$C(\tau) = \frac{1}{2} < \sum_{\varepsilon} \sum_{a_\varepsilon} \vec{\mu}^{(a_\varepsilon)}(t) \cdot \vec{\mu}^{(a_\varepsilon)}(t + \tau)$$

$$+ \sum_{\varepsilon} \sum_{b_\varepsilon} \vec{\mu}^{(b_\varepsilon)}(t) \cdot \vec{\mu}^{(b_\varepsilon)}(t + \tau)$$

$$- \sum_{a} \sum_{b} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t + \tau)> \qquad (3.8)$$

which simplifies to

$$C(\tau) = \frac{1}{2} <2 \sum_{\varepsilon} \sum_{a_\varepsilon} \vec{\mu}^{(a_\varepsilon)}(t) \cdot \vec{\mu}^{(a_\varepsilon)}(t + \tau)$$

$$- \sum_{a} \sum_{b} \vec{\mu}^{(ab)}(t) \cdot \vec{\mu}^{(ab)}(t + \tau)> \qquad (3.9)$$

The second term in (3.9) is of course, the pure intracollisional term whose treatment is similar to that of the pure intracollisional term, (2.10), in Chapter 2. It can be written in the temporal superposition approximation as

$$\langle\sum_{a}\sum_{b}\vec{\mu}^{(ab)}(t)\cdot\vec{\mu}^{(ab)}(t+\tau)\rangle$$

$$=\sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'}\, V\,\langle\vec{\mu}_i(t)\cdot\vec{\mu}_i(t+\tau)\rangle_i^{\varepsilon\varepsilon'} \qquad (3.10)$$

where $N_{\varepsilon\varepsilon'}$ is the total number of $\varepsilon\varepsilon'$ collisions per unit time per unit volume V, and $\langle\ldots\rangle_i^{\varepsilon\varepsilon'}$ denotes the collisional average of the dipole moments induced in $\varepsilon\varepsilon'$ collisions, over all $\varepsilon\varepsilon'$ collisions. Substitution of (3.10) into (3.9) yields

$$C(\tau)=\langle\sum_{\varepsilon}\sum_{a_\varepsilon}\vec{\mu}^{(a_\varepsilon)}(t)\cdot\vec{\mu}^{(a_\varepsilon)}(t+\tau)\rangle$$

$$-\tfrac{1}{2}\sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'}\, V\,\langle\vec{\mu}_i(t)\cdot\vec{\mu}_i(t+\tau)\rangle_i^{\varepsilon\varepsilon'} \qquad (3.11)$$

which reduces to

$$C(\tau)/V = \sum_{\varepsilon} n_\varepsilon \langle\vec{\mu}^{(a_\varepsilon)}(t)\cdot\vec{\mu}^{(a_\varepsilon)}(t+\tau)\rangle$$

$$-\tfrac{1}{2}\sum_{\substack{\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'}\langle\vec{\mu}_i(t)\cdot\vec{\mu}_i(t+\tau)\rangle_i^{\varepsilon\varepsilon'}\} \qquad (3.12)$$

We now introduce the temporal superposition approximation in the first term in (3.12). The total induced dipole moment in a particular molecule, a_ε, will be represented by a temporal superposition for the dipole moments induced in isolated binary collisions, that is

$$\vec{\mu}^{(a_\varepsilon)}(t) = \sum_i a_i \, \vec{\mu}_i \, (t-t_i)$$

where

$$\begin{aligned} a_i &= 1 \text{ for } \varepsilon\varepsilon' \text{ collisions, } \varepsilon' \neq \varepsilon \\ &= 0 \text{ for } \varepsilon\varepsilon \text{ collisions .} \end{aligned}$$

We then obtain

$$C(\tau)/V = \sum_\varepsilon \{ n_\varepsilon < \sum_{i,j} a_i \vec{\mu}_i (t-t_i) \cdot a_j \vec{\mu}_j (t+\tau-t_j) >$$

$$- \tfrac{1}{2} \sum_{\substack{\varepsilon' \\ \varepsilon \neq \varepsilon'}} N_{\varepsilon\varepsilon'} < \vec{\mu}_i(t) \cdot \vec{\mu}_i(t+\tau) >_i^{\varepsilon\varepsilon'} \} \qquad (3.13)$$

Taking out the intracollisional terms we obtain

$$C(\tau)_{\text{intra}}/V = \sum_\varepsilon \{ n_\varepsilon < \sum_i a_i^2 \vec{\mu}_i (t-t_i) \cdot \vec{\mu}_i (t+\tau-t_i) >$$

$$- \tfrac{1}{2} \sum_{\substack{\varepsilon' \\ \varepsilon \neq \varepsilon'}} N_{\varepsilon\varepsilon'} < \vec{\mu}_i(t) \cdot \vec{\mu}_i \, (t+\tau) >_i^{\varepsilon\varepsilon'} \}$$

$$= \sum_{\varepsilon} \{ n_\varepsilon \nu_\varepsilon \sum_{\substack{\varepsilon' \\ \varepsilon \neq \varepsilon'}} \langle a_i^2 \, \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) \rangle_i^{\varepsilon\varepsilon'}$$

$$- \tfrac{1}{2} \sum_{\substack{\varepsilon' \\ \varepsilon \neq \varepsilon'}} N_{\varepsilon\varepsilon'} \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) \rangle_i^{\varepsilon\varepsilon'} \} \qquad (3.14)$$

where ν_ε is the collision frequency of an ε molecule with all other molecules in the gas. In analogy to similar quantities defined in section 2.3, we write

$$\nu_\varepsilon = \sum_{\varepsilon'} N_{\varepsilon\varepsilon'}/n_\varepsilon \ . \qquad (3.15)$$

Since the quantity $\langle \ldots \rangle_i^{\varepsilon\varepsilon'}$ is a collisional average over $\varepsilon\varepsilon'$ collisions, the fraction of the coefficients a_i^2 that are non-zero is given by $u_{\varepsilon\varepsilon'}$, where $u_{\varepsilon\varepsilon'}$ is the relative frequency of $\varepsilon\varepsilon'$ collisions in the collision history of a molecule of species ε. Again, this quantity is closely related to the relative frequencies defined in section 2.3. We have

$$u_{\varepsilon\varepsilon'} = N_{\varepsilon\varepsilon'}/\sum_{\varepsilon'} N_{\varepsilon\varepsilon'} \ . \qquad (3.16)$$

Thus, we can write (3.14) as

$$C(\tau)_{\text{intra}}/V = \sum_{\substack{\varepsilon, \varepsilon' \\ \varepsilon \neq \varepsilon'}} [n_\varepsilon \nu_\varepsilon u_{\varepsilon\varepsilon'} - N_{\varepsilon\varepsilon'}/2]$$

$$\times \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) \rangle_i^{\varepsilon\varepsilon'} \ . \qquad (3.17)$$

Using (3.15) and (3.16), this reduces immediately to

$$C(\tau)_{\text{intra}}/V = \tfrac{1}{2} \sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon \neq \varepsilon'}} N_{\varepsilon\varepsilon'} \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \tau) \rangle_i^{\varepsilon\varepsilon'} \qquad (3.18)$$

In the case of a binary mixture this expression reduces to our previous result, (2.14), for the intracollisional autocorrelation function.

We now consider the intercollisional terms in (3.13),

$$C(\tau)_{\text{inter}}/V = \sum_{\varepsilon} n_{\varepsilon} \langle \sum_{\substack{i,j \\ i \neq j}} a_i \vec{\mu}_i(t - t_i) - a_j \vec{\mu}_j(t + \tau - t_j) \rangle . \qquad (3.19)$$

This can be rearranged into a sum of series, with one series for each species. The n^{th} term of each series expresses the correlation between the i^{th} and the $(i + n)^{\text{th}}$ collisions for that particular species:

$$C(\tau)_{\text{inter}}/V = \sum_{\varepsilon} n_{\varepsilon} \sum_{n} C_n^{\varepsilon}(\tau) \qquad (3.20)$$

where

$$C_n^{\varepsilon}(\tau) = \langle \sum_i [a_i \vec{\mu}_i(t-t_i) \cdot a_{i+n} \vec{\mu}_{i+n}(t + \tau - t_i - x_i)$$

$$+ a_{i+n} \vec{\mu}_{i+n}(t - t_i - x_i) \cdot a_i \vec{\mu}_i(t + \tau - t_i)] \rangle^{\varepsilon} \qquad (3.21)$$

where $x_i = t_{i+1} - t_i > 0$ is the interval between successive collisions, and $\langle \ldots \rangle^{\varepsilon}$ is the time average of the collision sequence of the ε molecule. Using a time average in the above expression, that is

$$\langle f \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T f(t)\, dt \, ,$$

we obtain

$$C_n^{\varepsilon}(\tau) = \lim_{T\to\infty} \frac{1}{T} \sum_i \left[C^{\varepsilon}_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau) + C^{\varepsilon}_{i,i+n}(x_i + \ldots + x_{i+n-1} + \tau)\right] \qquad (3.22)$$

with

$$C^{\varepsilon}_{i,i+n}(\tau) = \int_{-\infty}^{\infty} a_i \vec{\mu}_i(t) \cdot a_{i+n} \vec{\mu}_{i+n}(t - \tau)\, dt \qquad (3.22')$$

where the i's denote the collision variables of a molecule of species ε.

The expression on the right hand side of (3.22) is equal to the collision frequency, ν_{ε}, multiplied by the mean of the quantity in square brackets averaged over the time intervals $x_i, \ldots, x_{i+n-1}$ and over the collision variables $i, \ldots, i+n$. The average value of $C^{\varepsilon}_{i,i+n}(x_i + \ldots + x_{i+n-1} - \tau)$

over the collision variables is denoted by

$$\langle C^{\varepsilon}_{i,i+n}(x_i + \dots + x_{i+n-1} - \tau)\rangle_i$$

Then (3.22) can be written

$$\begin{aligned} C^{\varepsilon}_{n}(\tau) = \nu_{\varepsilon} \int_0^\infty \cdots \int_0^\infty & p(x_i,\dots,x_{i+n-1}) \\ & \times [\langle C^{\varepsilon}_{i,i+n}(x_i + \dots + x_{i+n-1} - \tau)\rangle_i \\ & + \langle C^{\varepsilon}_{i,i+n}(x_i + \dots + x_{i+n-1} + \tau)\rangle_i]\, dx_i \dots dx_{i+n-1} \end{aligned} \tag{3.23}$$

where $p(x_i,\dots,x_{i+n-1})$ is the probability distribution of the collision intervals $x_i,\dots,x_{i+n-1}$ for an ε molecule.

From our expression for the line shape function, (2.2), and (3.20), we obtain

$$W(\omega)_{\text{inter}}/V = \sum_{\varepsilon} n_{\varepsilon} \sum_{n} W^{\varepsilon}_{n}(\omega) \tag{3.24}$$

where

$$W^{\varepsilon}_{n}(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau} C^{\varepsilon}_{n}(\tau)\, d\tau. \tag{3.25}$$

It is now our task to evaluate the quantities $W^{\varepsilon}_{n}(\omega)$ appearing in (3.24) and sum the series to obtain a closed expression for the intercollisional line shape function per unit volume, $W(\omega)_{inter}/V$.

As in Chapter 2, to evaluate $W_n^{\varepsilon}(\omega)$ we choose an n, and consider all possible non-zero collision sequences that an ε molecule can undergo. By a non-zero collision sequence, we mean of course that at least two dipole moments are induced in that collision sequence. We evaluate each contribution of the different sequences separately, and then sum them to give $W_n^{\varepsilon}(\omega)$. In fact, we find that after evaluating $W_1^{\varepsilon}(\omega)$ and $W_2^{\varepsilon}(\omega)$, that the form of $W_n^{\varepsilon}(\omega)$ can be easily deduced.

Our derivation will closely parallel that of $W(\omega)_{inter}/V$ in the binary mixture case, performed in Chapter 2. The major difference in the two derivations is that for an arbitrary number of species there are many more possible collision sequences that a molecule can undergo. The details of collisional averaging will not be repeated here, and we evaluate the correlation coefficients $\langle\vec{\mu}_i \cdot \vec{\mu}_{i+n}\rangle_i$ by generalizing our previously obtained expressions to include the other terms that arise when an arbitrary number of species is considered.

Setting n = 1, we find that the contribution $W_1^{\varepsilon}(\omega)$ is due to collision sequences where an ε molecule undergoes two successive collisions with non-ε molecules. These sequences are shown schematically in Figure 3.1.

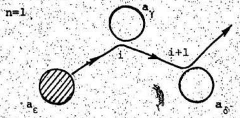

Figure 3.1: Collision sequences of a molecule of species ε for n=1.

Then from (3.25) and (3.23) we obtain

$$W_1^\varepsilon(\omega) = 2\nu_\varepsilon \ \mathrm{Re}\Big[\sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \tilde{p}_{\varepsilon\delta}(\omega)\ u_{\varepsilon\gamma} u_{\varepsilon\delta} \langle \vec{\mu}_i \cdot \vec{\mu}_{i+1} \rangle_i \Big] , \tag{3.26}$$

where

$$\tilde{p}_{\varepsilon\delta}(\omega) = \int_0^\infty e^{-i\omega x_i}\, p_{\varepsilon\delta}(x_i)\, dx_i \ , \tag{3.27}$$

and $p_{\varepsilon\delta}(x_i)$ is the probability distribution of collision intervals x_i for $\varepsilon\delta$ collisions. The quantities $u_{\varepsilon\gamma}$ and $u_{\varepsilon\delta}$ are respectively, the relative collision frequencies of $\varepsilon\gamma$ and $\varepsilon\delta$ collisions in the collision history of an ε molecule. $\langle \vec{\mu}_i \cdot \vec{\mu}_{i+1} \rangle_i$ denotes the averages taken over the collision variables of the relevant collisions. As mentioned previously, we will not explicitly derive them here, but deduce their form from our work on collisional averaging in Chapter 2 (specifically equations (2.32), (2.34), and (2.37)). We find that

$$\langle \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+1} \rangle_i = \int_0^\infty dc_{i+1} \int_0^\infty dc_i A_\varepsilon^\gamma (c_{i+1}) B_\varepsilon^\delta (c_{i+1} | c_i) P_\varepsilon (c_i) \tag{3.28}$$

where

$$A_\varepsilon^\gamma (c_1) = \int_0^\infty dc_1' \, A_\varepsilon^\gamma (c_1' | c_1)$$

with

$$A_\varepsilon^\gamma (c_1' | c_1) = \int_0^\pi d\xi \, \sin\xi \int_0^\infty dg \, \overline{\mu}(g,c) \cos \eta \, P_{\varepsilon\gamma} (g, \xi, c_1' | c_1) \tag{3.29}$$

and

$$B_\varepsilon^\delta (c_1' | c_1) = \int_0^\pi d\xi \sin\xi \int_0^\infty dg \, \overline{\mu}(g,c) \cos \eta' \, P_{\varepsilon\delta} (g, \xi, c_1' | c_1) \tag{3.30}$$

The collision variables $\{\vec{c}_1, c_1', \xi, \phi, g, \phi_g\}$, η and η' are as defined in Chapter 2. The quantities $P(g, \xi, c_1' | c_1)$ are the conditional probability distributions of g, ξ, and c_1' for a given c_1, subscripted for the appropriate collisions.

We note also that there now appears in our expression for $W_1^\varepsilon(\omega)$, (3.26), a double summation over non-ε molecules to take into account all possible non-zero collision sequences.

We now consider the contribution to the spectrum for n=2. $W_2^{\varepsilon}(\omega)$ is due to collision sequences in which an ε molecule initially collides with a non-ε molecule, experiences a second collision with any species, and then undergoes a third collision with a non-ε molecule. These sequences are depicted below.

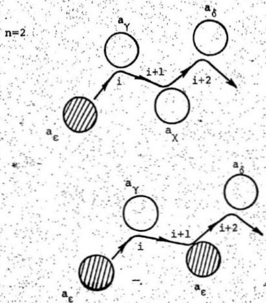

Figure 3.2 Collision sequences of a molecule of species ε for n=2.

From (3.25) and (3.23) we obtain

$$W_2^{\varepsilon}(\omega) = 2\nu_{\varepsilon} \mathrm{Re}[\sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \sum_{\chi} \tilde{p}_{\varepsilon\chi}(\omega)\, \tilde{p}_{\varepsilon\delta}(\omega)$$

$$\times\, u_{\varepsilon\gamma} u_{\varepsilon\chi} u_{\varepsilon\delta} \langle \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2} \rangle_i] \tag{3.31}$$

where $\langle \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2} \rangle_i$ again denotes the averages taken over the collision variables of the relevant collisions. From Chapter 2, using our given collision sequences we obtain

$$\langle \overline{\vec{\mu}}_i \cdot \overline{\vec{\mu}}_{i+2} \rangle_i = \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times\, A_\varepsilon^\gamma(c_{i+2})\, \Delta_{\varepsilon\chi}(c_{i+2}|c_{i+1})\, B_\varepsilon^\delta(c_{i+1}|c_i)\, P_\varepsilon(c_i). \tag{3.32}$$

where

$$\Delta_{\varepsilon\chi}(c_1'|c_1) = \int_0^\infty d\,\xi\, \sin\xi\, \cos\xi\, P_{\varepsilon\chi}(\xi, c_1'|c_1) \tag{3.33}$$

and $P_{\varepsilon\chi}(\xi, c_1'|c_1)$ is the conditional distribution of ξ, c' for given c_1 for $\varepsilon\chi$ collisions.

Using (3.32), we can rewrite (3.31) as

$$W_2^\varepsilon(\omega) = 2\nu_\varepsilon \mathrm{Re}[\sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \tilde{P}_{\varepsilon\delta}(\omega)\, u_{\varepsilon\gamma} u_{\varepsilon\delta} \int_0^\infty dc_{i+2} \int_0^\infty dc_{i+1} \int_0^\infty dc_i$$

$$\times\, A_\varepsilon^\gamma(c_{i+2}) [\sum_\chi \tilde{P}_{\varepsilon\chi}(\omega)\, u_{\varepsilon\chi} \Delta_{\varepsilon\chi}(c_{i+1}|c_i)]\, B_\varepsilon^\delta(c_{i+1}|c_i) P_\varepsilon(c_i)]. \tag{3.34}$$

Introducing the quantity

$$\Delta_\varepsilon(c_1'|c_1) = \sum_\chi \tilde{P}_{\varepsilon\chi}(\omega)\, u_{\varepsilon\chi} \Delta_{\varepsilon\chi}(c_1'|c_1) \tag{3.34}$$

in analogy to $\Delta_A(c_1'|c_1)$, (2.53), we obtain

$$W_2^{\varepsilon}(\omega) = 2\nu_{\varepsilon}\ \mathrm{Re} \sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \tilde{p}_{\varepsilon\delta}(\omega)\ u_{\varepsilon\gamma}u_{\varepsilon\delta} \int_0^{\infty} dc_{i+2} \int_0^{\infty} dc_{i+1} \int_0^{\infty} dc_i$$

$$\times\ A_{\varepsilon}^{\gamma}(c_{i+2})\ \Delta_{\varepsilon}(c_{i+2}|c_{i+1})\ B_{\varepsilon}^{\delta}(c_{i+1}|c_i)\ P_{\varepsilon}(c_i)]. \tag{3.36}$$

In general, we find that the nth contribution to the spectrum, $W_n^{\varepsilon}(\omega)$, has the form

$$W_n^{\varepsilon}(\omega) = 2\ \nu_{\varepsilon}\mathrm{Re}[\sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \tilde{p}_{\varepsilon\delta}(\omega)\ u_{\varepsilon\gamma}u_{\varepsilon\delta} \int_0^{\infty} dc_{i+n} \cdots \int_0^{\infty} dc_i \tag{3.37}$$

$$\times\ A_{\varepsilon}^{\gamma}(c_{i+n})\ \Delta_{\varepsilon}(c_{i+n}|c_{i+n-1})\ldots\Delta_{\varepsilon}(c_{i+2}|c_{i+1})\ \ B_{\varepsilon}^{\delta}(c_{i+1}|c_i)P_{\varepsilon}(c_i)],$$

which is a fairly obvious generalization of (2.55) for $W_n^A(\omega)$.

Then, from (3.37) and (3.24), we obtain for the intercollisional line shape function per unit volume,

$$W(\omega)_{\mathrm{inter}}/V = 2\sum_{\varepsilon} n_{\varepsilon}\nu_{\varepsilon} \sum_{\substack{\gamma,\delta \\ \gamma,\delta\neq\varepsilon}} \mathrm{Re}[\tilde{p}_{\varepsilon\delta}(\omega)u_{\varepsilon\gamma}u_{\varepsilon\delta} \sideset{}{'}\sum_{n=1}^{\infty} \tag{3.38}$$

$$\times \int_0^{\infty} dc_{i+n} \cdots \int_0^{\infty} dc_i A_{\varepsilon}^{\gamma}(c_{i+n})\Delta_{\varepsilon}(c_{i+n}|c_{i+n-1})\ldots B_{\varepsilon}^{\delta}(c_{i+1}|c_i)P_{\varepsilon}(c_i)]$$

We now wish to sum the series' in (3.38) to obtain a closed expression for $W(\omega)_{\text{inter}}/V$. The further a collision is removed from an arbitrarily chosen initial collision, i, the less correlated it is with that initial collision. Therefore it is reasonable to assume that $W_n^{\varepsilon}(\omega)$ diminishes rapidly enough with increasing n for the series in (3.38) to be convergent.

The quantity

$$\int_0^\infty dc_{i+n} \cdots \int_0^\infty dc_{i+2} A_\varepsilon^\gamma(c_{i+n}) \Delta_\varepsilon(c_{i+n}|c_{i+n-1}) \cdots \Delta_\varepsilon(c_{i+2}|c_{i+1})$$

in (3.38) is the n^{th} term in the Neumann expansion of the Fredholm equation

$$G_\varepsilon^\gamma(\omega, c\ ) = A_\varepsilon^\gamma(c_1) + \int_0^\infty dc_1' \Delta_\varepsilon(c_1'|c_1) G_\varepsilon^\gamma(\omega, c_1') \ . \qquad (3.39)$$

We have assumed that the Neumann expansions will be convergent, hence we obtain

$$W(\omega)_{\text{inter}}/V = 2 \sum_\varepsilon n_\varepsilon \nu_\varepsilon \sum_{\substack{\gamma,\delta \\ \gamma,\delta \neq \varepsilon}} \mathrm{Re}[\, \tilde{P}_{\varepsilon\delta}(\omega) u_{\varepsilon\gamma} u_{\varepsilon\delta}$$

$$\int_0^\infty dc_1' \int_0^\infty dc_1 G_\varepsilon^\gamma(\omega, c_1') B_\varepsilon^\delta(c_1'|c_1) P_\varepsilon(c_1)] \qquad (3.40)$$

We now derive an expression for the intracollisional line shape function per unit volume, $W(\omega)_{\text{intra}}/V$. Recalling our expression for the intracollisional autocorrelation function,

$$C(\tau)_{\text{intra}}/V = \tfrac{1}{2} \sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'} \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t+\tau) \rangle_i^{\varepsilon\varepsilon'} ,$$

and taking the Fourier transform of the above, we obtain

$$W(\omega)_{\text{intra}}/V = \tfrac{1}{2} \sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'} \langle \vec{\mu}_i(\omega) \cdot \vec{\mu}_i(-\omega) \rangle_i^{\varepsilon\varepsilon'} \tag{3.41}$$

where $\vec{\mu}_i(\omega)$ is the Fourier transform of the induced dipole moment $\vec{\mu}_i(\tau)$. Expression (3.41) reduces to

$$W(\omega)_{\text{intra}}/V = \tfrac{1}{2} \sum_{\substack{\varepsilon,\varepsilon' \\ \varepsilon\neq\varepsilon'}} N_{\varepsilon\varepsilon'} \langle \overline{\vec{\mu}}{}_i^2 \rangle_i , \tag{3.42}$$

upon using our approximation

$$\vec{\mu}_i(\omega) \simeq \vec{\mu}_i(0) = \int_{-\infty}^{\infty} \vec{\mu}_i(\tau)\, d\tau = \overline{\vec{\mu}}_i .$$

The quantity $\langle \overline{\vec{\mu}}{}_i^2 \rangle_i$ has been evaluated in Chapter 2, (2.64), and we obtain

$$\langle \overline{\vec{\mu}}{}_i^2 \rangle_i = \int_0^{\infty} dc_1 P_{\varepsilon}(c_1) \int_0^{\infty} dc_1' \, K_{\varepsilon}^{\varepsilon'}(c_1'|c_1)$$

where (3.43)

$$K_{\varepsilon}^{\varepsilon'}(c_1'|c_1) = \int_0^{\pi} d\,\xi \,\sin\xi \int_0^{\infty} dg\, \overline{\mu}^2 \, P_{\varepsilon\varepsilon'}(g,\xi,c_1'|c_1)$$

The line shape function for the collision-induced absorption spectrum is given by

$$W(\omega)/V = W(\omega)_{\text{intra}}/V + W(\omega)_{\text{inter}}/V \quad ,$$

thus combining (3.40), (3.42) with (3.43) yields

$$W(\omega)/V = \sum_{\substack{\varepsilon,\delta \\ \delta\neq\varepsilon}} \int_0^\infty dc_1 P_\varepsilon(c_1) \int_0^\infty dc_1' \{\tfrac{1}{2} N_{\varepsilon\delta} K_\varepsilon^\delta(c_1'|c_1)$$

$$+ 2n_\varepsilon \nu_\varepsilon u_{\varepsilon\delta} \sum_{\substack{\gamma \\ \gamma\neq\varepsilon}} \mathrm{Re}[\tilde{p}_{\varepsilon\delta}(\omega) u_{\varepsilon\gamma} G_\varepsilon^\gamma(\omega,c_1') B_\varepsilon^\delta(c_1'|c_1)]\}$$

$$= \sum_{\substack{\varepsilon,\delta \\ \delta\neq\varepsilon}} N_{\varepsilon\delta} \int_0^\infty dc_1 P_\varepsilon(c_1) \int_0^\infty dc_1' \{\tfrac{1}{2} K_\varepsilon^\delta(c_1'|c_1)$$

$$+ 2 \sum_{\substack{\gamma \\ \gamma\neq\varepsilon}} u_{\varepsilon\gamma} \mathrm{Re}[\tilde{p}_{\varepsilon\delta}(\bar{\omega}) G_\varepsilon^\gamma(\omega,c_1') B_\varepsilon^\delta(c_1'|c_1)]\} \quad . \qquad (3.44)$$

We now have an expression for the reduced line shape function for the collision-induced absorption spectrum of a gas mixture of arbitrary composition. No assumptions about the number of species, and the relative masses and mole fractions of these species have been made. Thus (3.44) should be generally applicable within the bounds of the underlying assumptions of the theory. The primary limitation is of course the low density restriction. However, as with the expression for $W(\omega)/V$ obtained in Chapter 2, application of (3.44) in its general form is extremely difficult, and we introduce a simplification to make computations easier.

3.3 Simplified Expression for the Line Shape Function

We employ the same approximation here as was used in section 2.7. That is, we will replace the quantities $\Delta_{\varepsilon\chi}(c_1|c_1)$ by their corresponding mean persistance-of-velocity ratio $\tilde{\Delta}_{\varepsilon\chi}$ as defined in (2.90). This approximation is discussed in greater detail in section 2.7 and in TIIE 2. Using the expression

$$\Delta_{\varepsilon\chi}(c_1'|c_1) = \tilde{\Delta}_{\varepsilon\chi}\delta(c_1'-c_1) \quad , \tag{3.45}$$

where δ is the Dirac delta function, in our expression (3.39) for Fredholm equations, we obtain

$$G^{\gamma}_{\varepsilon}(\omega,c_1) = A^{\gamma}_{\varepsilon}(c_1)/(1-\tilde{\Delta}_{\varepsilon}(\omega)) \tag{3.46}$$

where

$$\tilde{\Delta}_{\varepsilon}(\omega) = \sum_{\chi} \tilde{P}_{\varepsilon\chi}(\omega)\ u_{\varepsilon\chi}\tilde{\Delta}_{\varepsilon\chi} \quad . \tag{3.47}$$

Substituting (3.46) into (3.44) yields

$$W(\omega)/V = \sum_{\substack{\varepsilon,\delta \\ \delta\neq\varepsilon}} N_{\varepsilon\delta} \int_0^\infty dc_1 P_\varepsilon(c_1) \int_0^\infty dc_1 \{ \tfrac{1}{2} K_\varepsilon^\delta(c_1'|c_1)$$

$$+ 2 \sum_{\substack{\gamma \\ \gamma\neq\varepsilon}} u_{\varepsilon\gamma} \mathrm{Re}[\tilde{p}_{\varepsilon\delta}(\omega) A_\varepsilon^\gamma(c_1') B_\varepsilon^\delta(c_1'|c_1)/(1-\tilde{\Delta}_\varepsilon(\omega))]\} \qquad (3.48)$$

Introducing the quantities

$$C_\varepsilon^\delta = \tfrac{1}{2} \int_0^\infty dc_1 P_\varepsilon(c_1) \int_0^\infty dc_1' K_\varepsilon^\delta(c_1'|c_1) \qquad (3.49)$$

and

$$\alpha_\varepsilon^{\gamma\delta} = \int_0^\infty dc_1 P_\varepsilon(c_1) \int_0^\infty dc_1' A_\varepsilon^\gamma(c_1') B_\varepsilon^\delta(c_1'|c_1), \qquad (3.50)$$

we obtain

$$W(\omega)/V = \sum_{\substack{\varepsilon,\delta \\ \delta\neq\varepsilon}} N_{\varepsilon\delta} \{ C_\varepsilon^\delta + 2 \sum_\gamma u_{\varepsilon\gamma} \mathrm{Re}[\tilde{p}_{\varepsilon\delta}(\omega) \alpha_\varepsilon^{\gamma\delta}/(1-\tilde{\Delta}_\varepsilon(\omega))]\}. \qquad (3.51)$$

Expression (3.51) is applicable to mixtures of arbitrary composition. It holds for arbitrary numbers of species, arbitrary concentration ratios and arbitrary masses for those species. Like TIEE 1-5 it assumes pairwise additive central forces and induced dipole moments, and densities sufficiently low that temporal superposition is valid. Like the earlier work it is the result of a kinetic theory. Like TIEE 3 it neglects certain four-body correlations. On these points of comparison it represents the furthest development of the ideas on which the earlier work on intercollisional interference was based. Further development will require major extension of the foundations of the theory - to include some four-body correlations, for example, or noncentral forces, ternary and higher-order collisions and non-additive interactions, and even inelastic collisions.

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