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MOTIONAL NARROWING OF RAMAN Q-BRANCHES
OF GASEOUS N_2O PERTURBED BY ARGON GAS

A Thesis
Presented to
the Faculty of Graduate Studies
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Physics

by
Vivekanand Bissessur

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THE UNIVERSITY OF MANITOBA
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MOTIONAL NARROWING OF RAMAN Q-BRANCHES
OF GASEOUS N_2O PERTURBED BY ARGON GAS

BY

VIVEKANAND BISSESSUR

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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ABSTRACT

The shape, linewidth and shift of the isotropic part of the ν_1 and ν_3 vibrational Raman Q-branches of gaseous N_2O perturbed by argon gas have been studied. Starting with a fixed amount of N_2O at about 2 atm, the evolution of the Q-branch spectra is followed as the pressure of the perturbing gas is increased from about 2 to 140 atm. The lineshapes undergo frequency shift and exhibit motional narrowing which counteracts the usual collision broadening. The line-shape behaviour is analyzed and explained in terms of the indirect vibrational dephasing theory which was formulated by Neuman and Tabisz and applied to the Q-branches of pure N_2O gas. The experimental results and observations are successfully accounted for by the theory.

CONTENTS

	Page
ACKNOWLEDGEMENTS	i
ABSTRACT	ii
CHAPTER	
1 INTRODUCTION	1
1.1 General Remarks	1
1.2 Motional Narrowing	5
1.3 Motional Narrowing in Pure N ₂ O Gas	6
1.4 The Interest of N ₂ O-Ar Mixtures	9
2 THEORY	12
2.1 Vibrational Relaxation via Indirect Dephasing	12
2.2 Markovian Rotational Modulation	13
2.3 J-Scrambling Model	15
2.4 Construction of Rotational Stochastic Matrix	15
2.5 Rotational Relaxation Rate	18
2.6 Lineshape Formalism	19
2.7 Limiting Case of Rapid Relaxation	22
3 EXPERIMENTAL METHODS	25
3.1 Light Source	25
3.2 Gas Handling System	28
3.3 Optical System	29
3.3.1 The illumination optics	29
3.3.2 The collection optics	30
3.4 Monochromator	31
3.5 Detection and Recording System	32
3.6 Choice of Scattering Geometry	35
3.7 Measurement of the Slit Function	38
3.8 Measurement of Frequency Shifts	39

CHAPTER		Page
4	DATA ANALYSIS	42
	4.1 Correction for Instrumental Distortion of the Lineshapes	42
	4.2 Deconvolution of Measured Lineshapes	46
	4.3 Results of Linewidth Analysis	54
	4.4 Frequency Shift Analysis	54
	4.4.1 Peak frequency shifts of the ν_1 lineshapes	58
	4.4.2 Peak frequency shifts of the ν_3 lineshapes	59
5	DISCUSSION	68
	5.1 Possible Line-broadening Mechanisms	68
	5.2 Lineshape Analysis	71
	5.2.1 Generation of theoretical lineshapes	71
	5.2.2 Calibration of relaxation rate versus density	74
	5.2.3 Comparison between theory and experiment - ν_3 Q-branch	79
	5.2.4 Comparison between theory and experiment - ν_1 Q-branch	91
	5.3 Frequency Shift of Q-branch Lineshapes	104
	5.4 Effective Scrambling Diameter	110
	5.5 Comparison of Present Findings with Previous Work	113
6	CONCLUSIONS	116
	6.1 Indirect Vibrational Dephasing	116
	6.2 J-Scrambling Model	116
	6.3 Direct Dephasing	117
	6.4 Frequency Shift of Q-branch Lineshapes	117
	6.5 Effective Diameter for Rotational Scrambling	117
	APPENDIX	118
	REFERENCES	127

LIST OF FIGURES

Figure		Page
1.1	SCHEMATIC DIAGRAMS OF Q-BRANCH OF A LINEAR MOLECULE IN THE PRESENCE OF ROTATION-VIBRATION INTERACTION	3
3.1	SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS	26
3.2	POLARIZATION GEOMETRIES	36
4.1	SAMPLE DECONVOLUTION OF ν_1 LINESHAPE	50
4.2	SAMPLE DECONVOLUTION OF ν_3 LINESHAPE	52
4.3	SCHEMATIC ILLUSTRATION OF ν_1 FREQUENCY SHIFT ANALYSIS	58
4.4	SCHEMATIC ILLUSTRATION OF ν_3 FREQUENCY SHIFT ANALYSIS	62
5.1	COMPARISON OF THEORETICAL AND EXPERIMENTAL LINEWIDTH TRENDS - ν_3	76
5.2	COMPARISON OF THEORETICAL AND EXPERIMENTAL LINESHAPES - ν_3	81
5.3	COMPARISON OF THEORETICAL AND EXPERIMENTAL LINEWIDTH TRENDS - ν_1	92
5.4	COMPARISON OF THEORETICAL AND EXPERIMENTAL LINESHAPES - ν_1	94
5.5	COMPARISON OF THEORETICAL AND EXPERIMENTAL FREQUENCY SHIFT TRENDS - ν_1	105
5.6	COMPARISON OF THEORETICAL AND EXPERIMENTAL FREQUENCY SHIFT TRENDS - ν_3	107

LIST OF TABLES

Table		Page
4.1	DECONVOLUTED ν_1 Q-BRANCH LINEWIDTHS AT 294 K	55
4.2	DECONVOLUTED ν_3 Q-BRANCH LINEWIDTHS at 296 K	56
4.3	RAMAN SHIFTS OF PEAKS OF DECONVOLUTED ν_1 LINESHAPES	60
4.4	AVERAGE PEAK FREQUENCY SHIFTS OF DECONVOLUTED ν_1 LINESHAPES RELATIVE TO FREQUENCY OF Q(0)	61
4.5	RAMAN SHIFTS OF PEAKS OF DECONVOLUTED ν_3 LINESHAPES	66
4.6	AVERAGE PEAK FREQUENCY SHIFTS OF DECONVOLUTED ν_3 LINESHAPES RELATIVE TO FREQUENCY OF Q(0)	67

CHAPTER 1

INTRODUCTION

1.1 General Remarks

Raman scattering of light from molecular systems (gases, liquids, and solids) is a powerful and useful probe of molecular interactions and dynamics as well as of molecular structure and properties. For example, the intensity and polarization of the scattered light determine the polarizability of the molecular system and the frequency measurements at low pressures yield information about molecular structure. The linewidth, shift and shape of Raman spectra moreover furnish information about intermolecular interactions. In fluids, the lineshapes are not only determined by the intrinsic properties of the free molecule, but are also dependent on the perturbations exerted by other molecules. The effect of these external perturbations is usually to broaden and shift the spectral lineshapes; however, these same perturbations are also responsible for the narrowing of spectral lines. In contrast to line broadening, the phenomenon of line narrowing is much less common. The importance of any line broadening or narrowing mechanism is usually assessed through the linewidth. The complete lineshape, however, depends on the particular broadening (or narrowing) process or processes and the linewidth by itself does not necessarily tell one much about the wings of the line.

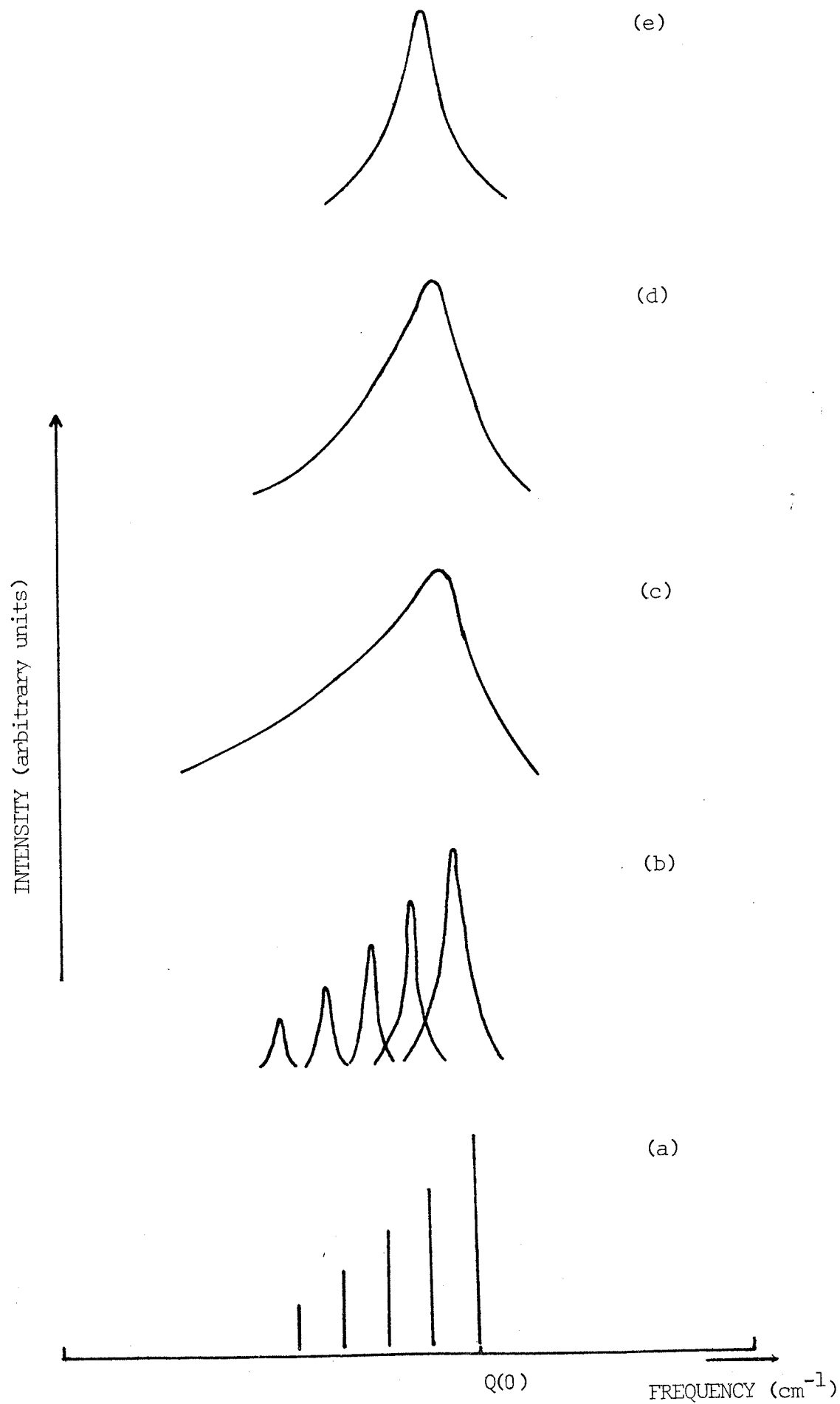
The broadening of the Raman lines in compressed gases is a consequence of intermolecular collisions which act to alter some aspects of molecular dynamics, such as phase or frequency, which characterize a particular Raman line. Rotationally inelastic collisions broaden the

rotational Raman lines. In a similar manner, vibrationally inelastic collisions may also modify the phase or frequency of vibrational motion and broaden the vibrational Raman lines or Raman Q-branches. These broadening effects may be termed as the direct effect of collisions on the Raman lineshapes. An indirect effect can also exist in the presence of rotation-vibration interaction. In the absence of collisions, this interaction splits a vibrational Q-branch into a band or series of discrete component lines, each corresponding to a particular rotational state characterized by the rotational quantum number J . Specifically, in a linear molecule, for each J the corresponding rotational line is shifted by $\alpha_e J(J+1)$ from the band origin, where α_e is the empirical rotation-vibration interaction constant. This is shown schematically in Fig.1.1(a). This implies that molecules in different rotational states have slightly different vibrational frequencies $Q(J)$. Rotationally inelastic collisions therefore cause the scattering molecule to emit at a fluctuating vibrational frequency and lead to a broadening of the components of the vibrational Q-branch as shown in Fig. 1.1(b). At high enough densities, the discrete component lines become collision-broadened to the point where they overlap, and the observed spectrum is a smooth envelope of the free-molecule spectrum; such is the case in the spectrum of the N_2O molecule. It is then practical to treat the Q-branch as a single broadened vibrational transition as displayed in Fig. 1.1(c) rather than as a multitude of independent transitions. At still higher densities, as we shall see, this same Q-branch might exhibit motional or collision narrowing (c.f. Figs.1.1(d) and (e)).

FIG. 1.1

SCHEMATIC DIAGRAMS OF Q-BRANCH OF A LINEAR
MOLECULE IN THE PRESENCE OF ROTATION-VIBRATION INTERACTION

The density of molecules increases from (a) to (e).



The definition of a Q-branch is now in order. The selection rule for rotational transitions accompanying a vibrational Raman transition for a linear molecule is given by

$$\Delta J = 0, \pm 2$$

The lines in the Raman spectrum comprise an S-branch ($\Delta J = +2$), a Q-branch ($\Delta J = 0$), and an O-branch ($\Delta J = -2$). Usually the Q-branch is an intense line that is unresolved in the rotational fine structure while the S- and O- branches form weak wings extending to lower and higher wave numbers, respectively, from this line.

1.2 Motional Narrowing

Motional narrowing was first observed by Bloembergen, Purcell and Pound¹ while studying the NMR spectrum of hydrogen. Theoretical discussions pertaining to the motional effect in NMR spectroscopy have been given by Anderson² and Kubo³. In optical spectroscopy, the most widely-studied sort of motional narrowing is Dicke narrowing⁴. This is the decrease in the normal Doppler width of a spectral line when the mean free path in the gas becomes less than or comparable to the wavelength of the emitted light. The narrowing is a manifestation of the effect of collisions on the translational states of the molecules, and within a certain density region, it becomes more pronounced with increasing density. Detailed studies of Dicke narrowing of rotational Raman lines in hydrogen have been reported by May and collaborators^{5,6,7} and by Clements and Stoicheff⁸, while narrowing of the vibrational line has been investigated by Murray and Javan⁹. The complementary phenomenon of collisional broadening was also studied in some of these experiments.

Besides Dicke narrowing, which has to do only with the translational degrees of freedom, other sorts of motional narrowing arise, for example, from the collapse of rotational structure in the lineshapes. One example is the orientational broadening of depolarized Rayleigh and Raman lineshapes that occurs at liquid densities¹⁰. This involves the collapse of rotational O- and S- branch structure about the central frequency. The paradoxical use of the term broadening in such a case is due to the narrowing of the O- and S- branches which appears as broadening of the Q-branch. Another, less widely-studied example is the collapse of rotational structure within the Q-branch itself. Dion and May¹¹ have shown that the Raman Q-branch lines of HD at room temperature exhibit this kind of motional narrowing with increasing density. They interpreted their results with limited success in terms of the theory of motional narrowing of Alekseev and Sobel'man¹². Later Witkowitz and May¹³ studied the collisional effects in compressed HD at room temperature and at 85K. At low densities they found evidence of collision broadening. At medium and higher densities they observed the motional narrowing of the Q-branch and used the approach of Alekseev and Sobel'man to account for the observed lineshapes, but an agreement was obtained only after introducing fitted parameters into the theory.

1.3 Motional Narrowing in Pure N₂O Gas

During recent studies of vibrational relaxation in dense gases, Neuman and Tabisz^{14,15} found evidence of motional narrowing, owing to collapse of rotational structure, in the ν_1 and ν_3 Raman Q-branches of

pure N_2O gas. The rotation-vibration coupling in N_2O defines the Q-branch structure of the ν_1 and ν_3 bands. This interaction broadens the vibrational Q-branch in the free molecule limit (at very low densities). With increasing density, the effect of collisions assumes greater importance. At high enough densities or collision rates, they affect the Raman Q-branches in an indirect way by modulating the rotation-vibration interaction, thus leading to the collapse of the Q-branch lineshape about its central frequency--this is the narrowing phenomenon. The broadening of the lineshapes can still occur directly if collisions affect the vibrational motions as well as indirectly through rotation-vibration coupling, and indeed, the broadening of the lineshapes was observed at higher densities.

Neuman and Tabisz interpreted the motional narrowing as the result of a vibrational dephasing process arising indirectly from collision-induced rotational relaxation. In other words, molecular collisions without affecting the vibrational behaviour directly, nonetheless cause vibrational frequency changes indirectly by inducing transitions between rotational states with which the vibration is coupled. In particular, the dephasing was assumed to arise from the random modulation of the vibrational resonance frequency and, more specifically, this frequency modulation was assumed to be a Markovian stochastic process. On a physical basis, the vibrational mode or Q-branch in question is pictured as an oscillating "system" in contact with a thermal "bath" of random perturbers. The system is adiabatically perturbed by the bath so that the system frequency is a definite function of the instantaneous bath state and is modulated by bath-state transitions. If these may be

described as Markovian, that is, if dynamic-coherence effects during transitions are unimportant, then the system frequency likewise behaves as a Markov process. In the case of N_2O where there is modulation of vibrational frequency due primarily to rotational transitions occurring during collisions, the vibration is therefore regarded as immersed in a "rotational bath", and the collisional modulation of the rotational state is treated as a Markovian process. In this context, Neuman and Tabisz successfully applied the lineshape theory of Anderson and Kubo to account for the narrowing of the Q-branch lineshapes with increasing density; this theory had first been applied to a stochastically perturbed oscillator in NMR spectroscopy.

In order to apply the lineshape theory of Anderson² and Kubo³, it is essential to devise a method for defining the transition probabilities between the bath states. Accordingly, Neuman and Tabisz used a scheme of transition probabilities between rotational states which they called the "J-scrambling model". In this model, when the vibrating molecule collides with a perturber, its rotational state is totally scrambled or thermalised. That is, the probability of its emerging from the collision in a given J-level is the same, namely, the ordinary thermal probability of that level, regardless of the value of J the vibrating molecule had just before collision.

It is a particular feature of any oscillator undergoing Markovian frequency modulation, owing to its interaction with a thermal bath, that its spectral linewidth would experience asymptotic narrowing with large increase in modulation or relaxation rate. Specifically, the linewidth of its power spectrum is inversely proportional, for rapid enough relaxation, to the thermal relaxation rate of the bath state^{14,16}. Neuman and

Tabisz, in spite of ignoring the effect of direct dephasing, nevertheless succeed quite well in accounting for the narrowing of the lineshapes. At high densities where collisional broadening due to direct dephasing takes over, their theoretical treatment does not apply because it excludes any direct dephasing. In this context, direct dephasing is the result of the various adiabatic multipolar interactions between colliding N_2O molecules and not because of energy relaxation of the vibrational mode in question.

1.4 The Interest of N_2O -Ar Mixtures

Evidence of motional narrowing of the ν_1 and ν_3 Raman Q-branches of N_2O in gaseous mixtures with argon has been reported by Ouillon¹⁷, but no quantitative interpretation of the narrowing effect in terms of any existing lineshape theory was made. In the present work, we consider the experimental study and subsequent theoretical treatment of the motional narrowing of the isotropic spectra of the ν_1 and ν_3 Raman Q-branches of gaseous N_2O perturbed by argon gas. One of our aims is to keep the N_2O concentration at a level where the effect of any N_2O - N_2O interaction is negligible, so that all perturbation of the N_2O vibrational modes is essentially due to interaction with argon atoms. The argon atom as a perturber is particularly significant since it is spherical and possesses no permanent electric moments. Although this does not totally preclude all multipole interactions between colliding N_2O molecules and argon atoms, we expect any direct dephasing of the vibrational modes to be delayed until we have a considerable density of perturbers. We note that indirect de-

phasing is also believed to arise from some sort of electric multipole interactions. In our experiments, we anticipate indirect dephasing to feature predominantly, and the earlier work of Ouillon¹⁷ which reports narrowing of the Q-branches up to a high density of perturbers lends support to our expectations. In this work, we shall not consider the details of various multipolar interactions which give rise to dephasing.

From the foregoing considerations, we would expect the motional narrowing to persist up to higher pressures than in the case of pure N_2O where it is masked and subsequently overtaken by the usual collisional broadening at an earlier stage. This situation is hence amenable to theoretical analysis using the approach of Neuman and Tabisz. As they have done, we shall use the theory of Anderson and Kubo to account for the Q-branch lineshape behaviour with increasing density and employ a rotational relaxation scheme based on the J-scrambling model. Comparison between theory and experiment would then not only test the validity of the lineshape theory of Anderson and Kubo as applied to Raman Q-branches, but would also test the particular scheme of rotational relaxation, notably the J-scrambling model.

We shall also undertake the measurement of any pressure shift of the ν_1 and ν_3 bands. At low pressures, because of its skewed shape owing to rotation-vibration interaction, a given Q-branch spectrum has a peak frequency which differs from the thermal average frequency ω_0 . With increasing pressure, however, the spectrum narrows and its peak gradually shifts in frequency and ultimately coincides with ω_0 , that is, the spectrum

collapses about its central frequency ω_0 . This pressure-dependent peak frequency shift which is clearly predicted by the indirect-dephasing theory has not been studied experimentally so far.

On the whole, it is hoped that the present work would test the status of the indirect vibrational dephasing mechanism mediated via rotation-vibration coupling as a possible explanation of the narrowing of the Raman Q-branches of N_2O gas. The information obtained should add to our knowledge about the dynamics and interactions of the linear N_2O molecule.

Chapter 2 deals with the essential details of the indirect vibrational dephasing theory in terms of which the experimental Q-branch spectral profiles will be interpreted. In Chapter 3, the experimental aspects of the present work are presented. The methods of analysis of the experimental results and the relevant data are given in Chapter 4. A discussion of the experimental findings with regard to the indirect-dephasing theory follows in Chapter 5. Finally, the last chapter summarizes the main conclusions that are reached. The thesis ends with an appendix and a list of references.

CHAPTER 2

THEORY

In this chapter, the essential details of the indirect vibrational dephasing theory formulated by Neuman and Tabisz^{14,15,18} are presented. We describe the theoretical framework which would ultimately enable us to apply the lineshape theory of Anderson² and Kubo³ to the Q-branch lineshape problem.

2.1 Vibrational Relaxation via Indirect Dephasing

For many purposes, it is useful to divide the many degrees of freedom in molecules into two groups, a part of primary importance and a part of secondary importance. In other words, we may say that the molecule has some degrees of freedom or modes that we excite and many others that are not excited directly but interact with the excited modes. Accordingly, the modes of primary importance form a subsystem in the molecule while the remaining modes, that is, the modes of secondary importance make a large system that functions as a "heat bath" for the former. The bath here is entirely intramolecular. For our present purposes, the "system" is a single vibrational mode abstracted from the other molecular degrees of freedom. It vibrates with eigenfrequencies that are randomly modulated by interaction with a "bath". The bath state is assumed to depend only on rotational quantum numbers, and therefore for a linear molecule, only on the quantum number J of the vibrating molecule itself. Thus, in this context, the possible bath states are identified as the J -levels of the vibrating molecule. There is no significant coupling of the vibrational

frequencies to any other quantum number besides J . The system-bath interaction is assumed adiabatic, that is, there are no changes in quantum number of the vibrational mode in question. This presumes that energy relaxation of this mode is negligible. All vibrational relaxation is assumed to be due to dephasing.

We can visualise the dephasing process as follows. When the vibrating molecule collides with a perturber molecule, the former undergoes a rotational transition. Its vibrational transition frequencies change as a secondary result, because of the J -dependence of vibrational frequency, that is, because of rotation-vibration coupling. The time-integrated effect of these frequency fluctuations eventually leads to the loss of vibrational phase coherence (dephasing). The collisions are taken as instantaneous; between collisions, the molecule is assumed to vibrate at exact free-molecule eigenfrequencies. The vibrational phase resumes just after collision with the same value it had just before. Thus, all dephasing occurs between collisions, and none during collisions. The dephasing is attributed entirely to the indirect effect eventually produced by collisions through internal rotational transitions. Any direct dephasing immediately resulting from external perturbation is discounted.

2.2 Markovian Rotational Modulation

From the assumptions of §2.1, it is clear that the scheme of collision-induced rotational transitions plays a key role in the vibrational dephasing. Since the times and outcomes of collisions can be predicted only statistically, the history of the rotational bath is accordingly

treated as a stochastic process. The scheme of rotational transition probabilities is assumed to be Markovian. That is, the probability for any given "outgoing" J-level to follow a collision depends at most on the "incoming" J-level just prior to collision, and not on any antecedent history.

The Markovian modulation process is completely specified by a set of relaxation parameters c_j , the decay constant (inverse lifetime) of the j^{th} rotational level, and p_{jk} , the conditional probability that, upon leaving the j^{th} level, the molecule enters the k^{th} . This information is encoded in the rotational "stochastic matrix" D defined by

$$D_{jk} = \begin{cases} c_j & , j=k \\ -c_j p_{jk} & , j \neq k \end{cases} \quad (2.1)$$

in which form it enters the lineshape formalism described below in §2.6. We are thus faced with specifying the c_j and p_{jk} . In the present study, we shall be dealing with the case of N_2O (in gaseous mixtures with argon) at room temperature where there are some 55 J-levels that are significantly populated. Hence, there is a very large number of relaxation parameters to be dealt with. To calculate all these ab initio is very difficult. We therefore resort to some physical model whereby we impose constraints on the relaxation parameters and reduce the number of independent ones. This model which was used by Neuman and Tabisz in the analysis of vibrational relaxation in pure N_2O gas^{14,15} is described in the following section.

2.3 J-scrambling Model

The model chosen is the simplest possible and is the J-scrambling model mentioned in Chapter 1. In this model, when a vibrating molecule collides with a perturber, its rotational level is totally scrambled or thermalised. The probability of its emerging from the collision in a given J-level is the same, namely, the ordinary thermal probability of that level regardless of the incoming value of J. Besides being simple, this model is chosen because it is also the physical basis of the Gordon "J-diffusion" model¹⁹. The Gordon model has been extensively used in the analysis of anisotropic light scattering in order to obtain information about the reorientational motion of linear molecules. It is significant that the same physical model can be applied to both reorientational behaviour and vibrational dephasing, and thus used to predict both the anisotropic and isotropic Raman lineshapes. As stated in Chapter 1, in the present work only the study of the isotropic Raman spectra is undertaken because it is the isotropic part of the Raman scattering that furnishes information on vibrational relaxation directly.

2.4 Construction of Rotational Stochastic Matrix

The relative values of the conditional transition probabilities p_{jk} appearing in (2.1) are obtained from the assumptions that (a) complete thermal relaxation of the rotational state (J-level) occurs at every collision and (b) no additional relaxation occurs (between collisions). For a fixed incoming state j , the p_{jk} then satisfy

$$p_{jk} \propto f_k \text{ as } k \text{ varies.}$$

f_k is the thermal probability of level k . With the normalisation conditions

$$\sum_{k(\neq j)} p_{jk} = 1 \quad \text{and} \quad \sum_k f_k = 1,$$

it follows that

$$p_{jk} = f_k / (1 - f_j) \quad (2.2)$$

An estimate of the decay constants c_j of the various rotational levels may be obtained from our physical assumptions. The lifetimes c_j^{-1} must be on the order of τ_{BC} , the time between binary collisions. In view of the fact that the model includes the probability that a molecule will emerge from a collision in the same J -level it arrived in, and this probability is different for the various J -levels, the lifetimes c_j^{-1} will therefore vary from state to state. The more probable states will have longer lifetimes. Moreover, the c_j^{-1} may differ systematically from the kinetic theory value of τ_{BC} because the effective cross-section for rotational scrambling may differ from the kinetic-theory cross-section.

An obvious requirement of physical self-consistency is now invoked, namely, the principle of detailed balance in order to find the exact relative magnitudes of the c_j . Detailed balance implies that the probability flux out of level j must be equal to the total flux into j from all other levels k in order to maintain thermal equilibrium. We therefore have

$$f_j c_j = \sum_{k(\neq j)} f_k c_k p_{kj} \quad (2.3)$$

Upon substitution of $p_{kj} = f_j/(1-f_k)$, we obtain

$$f_j c_j = \sum_{k(\neq j)} f_k c_k f_j / (1-f_k)$$

from which

$$c_j = \sum_{k(\neq j)} f_k c_k / (1-f_k).$$

Defining

$$r \equiv \sum_k f_k c_k / (1-f_k),$$

we obtain for the last equation

$$c_j = r - f_j c_j / (1-f_j),$$

whence

$$c_j = r (1-f_j) \quad (2.4)$$

This fixes the relative magnitudes of the c_j . The value of r cannot be determined from the foregoing equilibrium criterion which only provides us with a set of homogeneous equations in the c_j . Thus, detailed balance cannot be used to determine the c_j uniquely.

From the formulae (2.1), (2.2) and (2.4), we can now write down the

resultant stochastic matrix

$$\underline{D} = r \begin{bmatrix} 1-f_1 & -f_2 & -f_3 & \dots \\ -f_1 & 1-f_2 & -f_3 & \\ -f_1 & -f_2 & 1-f_3 & \\ \vdots & & & \ddots \end{bmatrix} \quad (2.5)$$

where f_j is the thermal probability of the j^{th} rotational level.

2.5 Rotational Relaxation Rate

As will be shown below, r in equation (2.5) may be identified as the rotational relaxation rate mentioned in Chapter 1. In fact, it is the only free parameter in the model ultimately to be determined by a fit to the experimental data. Since the D -matrix as a whole is proportional to r , any adjustment of r affects the model by altering the overall speed of rotational relaxation without otherwise changing its history. The probability of a scrambling event within a short time Δt is $r \Delta t$, and $r \Delta t(1-f_j)$ is the combined probability that scrambling will occur and will cause the molecule to leave its previous (j^{th}) rotational level. It then follows that the decay constant (inverse lifetime) for the j^{th} rotational state is $r(1-f_j)$. This is precisely what was stated in (2.4).

The parameter r may be interpreted as the binary collision rate where by "collision" we mean any encounter close enough to scramble the rotational state. We therefore expect r , like the various c_j , to be similar--if not equal--to the kinetic-theory value of τ_{BC}^{-1} . In view of its collision-rate interpretation it is natural to expect r to be

proportional (at a fixed temperature) to the number density n of gas molecules just like the kinetic-theory collision rate τ_{BC}^{-1} . The assumption that binary collisions induce relaxation may be put to test by the prediction

$$r \propto n \quad (2.6)$$

To that end, we are left with two possibilities. We may check if (2.6) is satisfied by fitting values of r to the measured lineshapes at various densities. Alternatively, we may find the proportionality constant in (2.6) and proceed therefrom to find values of r and corresponding theoretical lineshapes for the various experimental densities and compare theoretical and measured lineshapes. The latter method has been used in earlier work on pure N_2O gas^{14,15} and the same method will be applied here to the N_2O -Argon mixtures. In the next section, we describe the lineshape formalism which incorporates the stochastic matrix $\underline{D}$.

2.6 Lineshape Formalism

In §2.2 it was postulated that molecular vibration is subjected to a Markovian frequency modulation provided that (a) the instantaneous vibrational frequency depends only on the rotational state of the molecule, and (b) rotational transitions themselves represent a Markov process. We now outline Kubo's³ derivation of the power spectrum of an oscillator undergoing Markovian frequency modulation.

Since we consider only the isotropic part of the Raman scattering, we begin by a formal relationship between the isotropic power spectrum and the time dependence of molecular variables. Specifically, the isotropic vibrational scattering spectrum²⁰ in terms of the vibrational autocorrelation function is given by:

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle q(0)q(t) \rangle \quad (2.7)$$

where classically, q is the oscillator displacement; quantum-mechanically it is a matrix element of the displacement taken between lower- and upper-state vibrational eigenfunctions. Either way, $q(t)$ oscillates with the classical resonance frequency or with the Bohr transition frequency between upper and lower states. $q(t)$ is written in terms of the analytical signal as

$$q(t) \propto \text{Re} \{ \exp i(\omega_0 t + \eta(t) + \theta) \} , \quad (2.8)$$

where ω_0 is the mean resonance frequency, $\eta(t)$ is a random phase shift accruing by time t (this takes account of the random modulation of the resonance frequency about ω_0), and θ is the initial phase (which is randomly distributed in an ensemble of independent oscillators). Now, with the definition of the "relaxation function" $\phi(t)$ as the ensemble average

$$\phi(t) = \langle e^{i\eta(t)} \rangle ,$$

we can write (2.7) as

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{-i\omega t} (e^{i\omega_0 t} \phi(t) + \text{C.C.}) \quad (2.9)$$

The lineshape problem is thus reduced to finding the relaxation function. We note that so far the formula for $I(\omega)$ applies to any scheme of frequency modulation. For present purposes, we need the form of $\phi(t)$ for the particular case of Markovian modulation. We let $\omega_0 + \omega_j$ be the vibrational resonance frequency associated with the j^{th} rotational level, and let Ω denote the matrix $(\omega_j \delta_{jk})$. Then, for Markovian rotational modulation it is found that

$$\phi(t) = \vec{f} \cdot \exp(i\Omega - D) t \cdot \vec{e}, \quad (2.10)$$

where $\vec{f}$ is the row vector formed by the thermal weights f_j , $\vec{e}$ is the column vector ${}^t(1,1,\dots)$, and D is the rotational stochastic matrix¹⁴. Substituting for $\phi(t)$ in (2.9), we obtain the lineshape formula

$$I(\omega) \propto \vec{f} \cdot \text{Re} \{ [i((\omega - \omega_0) \tilde{E} - \tilde{\Omega}) + \tilde{D}]^{-1} \} \cdot \vec{e}, \quad (2.11)$$

where $\tilde{E}$ is the unit matrix. This is the formula which will be used at length to generate the theoretical lineshapes. The lineshape formula clearly expresses the relation of the lineshape to the relaxation rate of the bath (as described by the stochastic matrix $\tilde{D}$) and to the nature of the spectrum (as described by $\vec{f}$ and $\tilde{\Omega}$).

2.7 Limiting Case of Rapid Relaxation

It was stated in Chapter 1 that, in the regime of high enough relaxation rate, the Q-branch lineshape collapses about its central frequency ω_0 . The aim here is to show that the lineshape formalism developed in §2.6 does in effect correctly predict the collapse of the lineshape about ω_0 .

From (2.4), it is clear that as the relaxation rate becomes more and more rapid, the decay constants c_j become proportionally larger to the point where the stochastic matrix $\underline{D}$ overwhelms $\underline{\Omega}$ in (2.10). It then follows that

$$\begin{aligned}\phi(t) &\sim \vec{f} \cdot \exp(-\underline{D}t) \cdot \vec{e} \\ &= \vec{f} \cdot (\underline{E} - \underline{D}t + \frac{1}{2} \underline{D}^2 t^2 - \dots) \cdot \vec{e}\end{aligned}\tag{2.12}$$

In order to proceed further, we now evaluate the dot product:

$$\begin{aligned}\vec{f} \cdot \underline{D} &= \sum_k f_k D_{kj} \\ &= f_j c_j - \sum_{k(\neq j)} f_k c_k D_{kj}\end{aligned}$$

From (2.3), we find that

$$\vec{f} \cdot \underline{D} = 0$$

Thus, the dot product of $\vec{f}$ with any power ≥ 1 of $\underline{D}$ is zero so that (2.12) may be written as

$$\phi(t) \sim \vec{f} \cdot \underline{E} \cdot \vec{e} = 1,$$

i.e. $\phi(t)$ is approximately constant. The Fourier transform of $\phi(t)$ may then be written as

$$F \phi(\omega) \propto \delta(\omega) \quad (2.13)$$

Now, denoting $F f(\omega)$ as the Fourier transform of a function $f(t)$:

$$\text{i.e. } F f(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} f(t)$$

and using the following general properties of Fourier transforms:

$$F (e^{i\omega_0 t} f) (\omega) = F f(\omega - \omega_0)$$

$$\text{and } F (f^*) (\omega) = (F f)^*(-\omega),$$

we can rewrite (2.9) as

$$I(\omega) \propto F \phi(\omega - \omega_0) + (F \phi)^*(-\omega - \omega_0) \quad (2.14)$$

From (2.13) and (2.14), we then obtain

$$I(\omega) \propto \delta(\omega - \omega_0) + \delta(-\omega - \omega_0) \quad (2.15)$$

Hence, we find that in the regime of rapid relaxation, the lineshape collapses about $|\omega| = \omega_0$. This is the motional narrowing discussed in

Chapter 1. The relation (2.15) is consistent with the statement that the linewidth of the power spectrum is asymptotically proportional to the relaxation rate, provided that the bath-state modulation is Markovian. However, it does not explicitly define the lineshape behaviour during the approach to a δ -function.

The conclusion that may be drawn is that the lineshape formalism of §2.6 satisfies our expectations in the limit of rapid relaxation.

CHAPTER 3

EXPERIMENTAL METHODS

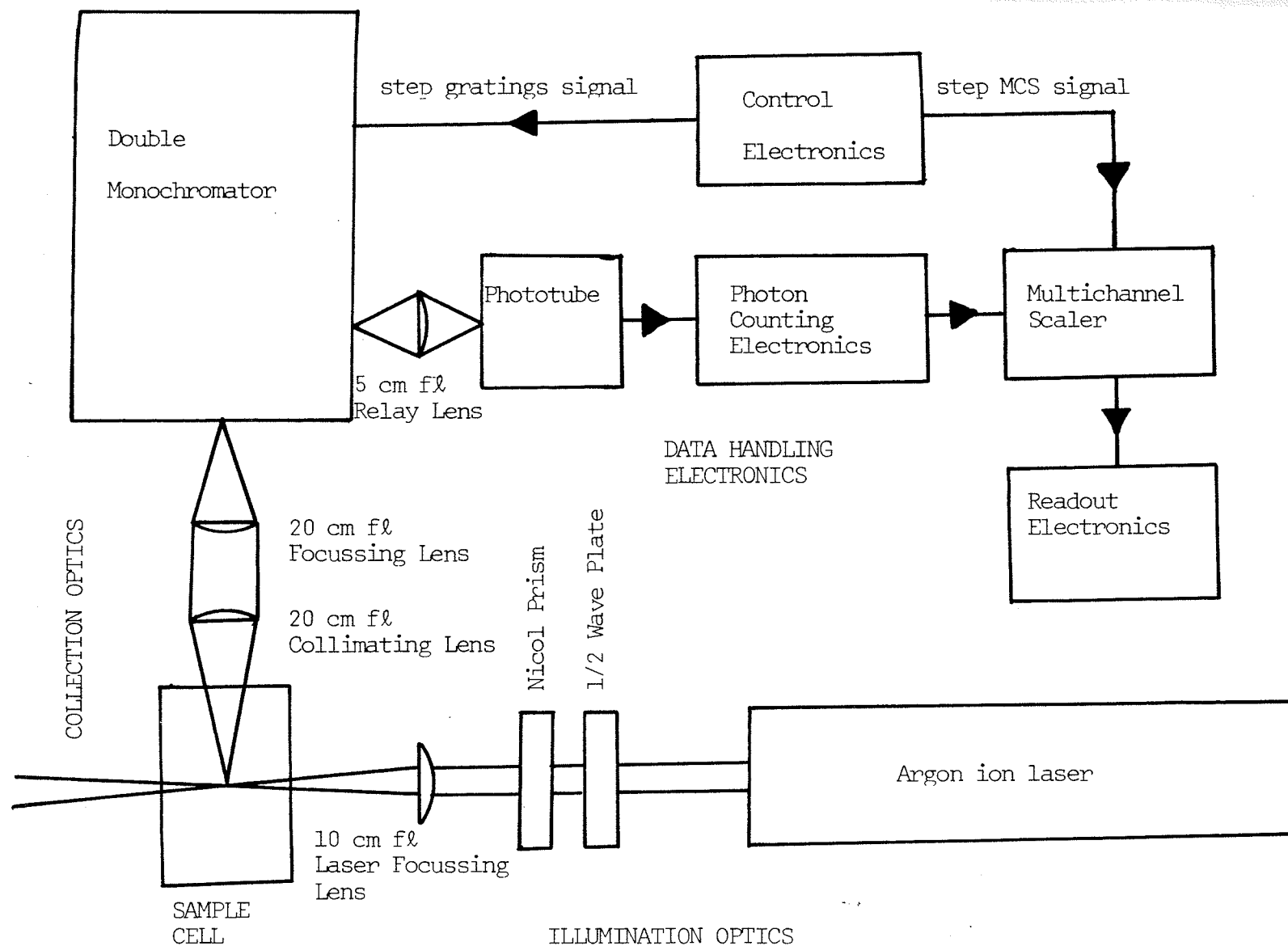
The apparatus was a typical laser-Raman system used for light scattering studies. Its essential components were a light source, a gas-handling system, a monochromator, an optical system as well as a detection and recording system. Light from a laser was sent through a gas sample. The light scattered at right angles to the incident beam was collected and analyzed by a monochromator. The output signal was then detected and recorded by photon-counting electronics. A block diagram of the laser-Raman set-up is shown in Fig. 3.1. The operation of the various components and the measurement techniques are described below.

3.1 Light Source

An argon ion laser (Coherent Radiation model CR-6 SG) was used as the light source. The laser light was linearly polarized with the electric vector vertical to the direction of propagation by means of a Brewster window. The laser was also equipped with an internal prism that allowed operation at a single laser line. The 4880 Å line was used for excitation. In order to optimize the scattered intensity which increases as ν^4 , the 4880 Å laser line was chosen over the equally bright 5145 Å line. The excitation line had a spectral width (Full Width at Half Maximum, FWHM) of about 0.1 cm^{-1} . Under normal operating conditions, the laser output power was typically of the order of 1 W. The laser power was kept stable during the recording of spectra by operating the laser-tube on the "light regulation" mode; this included a

FIG. 3.1

SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS



feedback mechanism whereby the laser-tube current was regulated by the externally-monitored intensity of the beam.

3.2 Gas Handling System

The gas handling system consisted of a sample cell and its associated high-pressure equipment. The sample cell was essentially a solid stainless steel block cross-bored with 1" diameter holes. The cell and its associated plumbing were constructed by American Instrument Corp. (AMINCO) and could withstand pressures up to 750 atm. A Bourdon-tube gauge (Heise Model CM-11170) was used to measure the sample pressure. A blackened aluminum liner was fitted inside the cell in order to reduce stray light. The cell was furnished with three fused silica windows which did not cause depolarization of the laser beam. All the experiments were performed at room temperature as the cell was not equipped with any means of sample temperature control.

The sample (N_2O -Ar mixture) was of chemical-grade purity (99.0%). Both the N_2O and argon were supplied by Matheson of Canada Ltd. In order to remove traces of other gases, the cell was first flushed several times with pure N_2O and then charged with about 2 atm of N_2O gas. Argon gas was then allowed in the cell in stages as experiments were performed at successively higher pressures. For the purpose of minimizing the elastic Tyndall scattering of the exciting radiation by dust particles, the passage to the gas cell was fitted with a series of sintered-metal filters which rejected any particles larger than 5 μm . Moreover, the sample was left undisturbed overnight after gas was let into or out of the cell in order to allow enough time for any particulate matter to settle out

before experimentation. By so doing, stability of the sample temperature was also achieved. The precaution taken was not a complete solution to either problem, since local heating in the laser beam could perturb the temperature and give rise to convection currents in the sample. Dust particles are mainly troublesome near the Rayleigh line insofar as the intensity of the Tyndall scattering fluctuates as the dust particles float randomly through the laser beam. In the experiments, no measurements were made close to the Rayleigh line and therefore, any dust particles left over in the cell did not pose a serious problem. Furthermore, any gaseous impurities, though usually a problem near the Rayleigh line, were not cause for concern in view of the fact that it is generally unlikely that an impurity will scatter at the same Raman vibrational frequencies as the sample.

3.3 Optical System

The optical system may be conveniently divided into two parts:

(a) the illumination optics and, (b) the collection optics (See Fig.3.1). Since Raman scattering is very weak, especially in gases, it is necessary to use the most efficient illumination and collection optics. Several workers^{21,22,23} have given the conditions for the optimum optical arrangements for Raman spectroscopy. In our laser-Raman set-up care had been taken to comply with these conditions as far as possible.

3.3.1 The illumination optics

The laser beam was directed towards the sample cell by a series

of glass prisms. A half-wave plate rotated the laser beam polarization from the vertical to the correct polarization. Any extraneous polarization was then eliminated by means of a Nicol prism. The beam was finally brought to a focus inside the sample cell by means of a 10 cm f.l. lens in order to increase the illumination in the cylindrical scattering volume from which the light scattering was detected. Studies have shown that the increased radiance of the focussed laser beam substantially enhances the quality of Raman spectra^{21,22}. Accordingly, a stronger focussing lens might have served the purpose better, but the construction of the cell mounting restricted the minimum focal length of the lens to be about 10 cm. It should be mentioned that stronger focussing would also give rise to some loss of polarization definition of the laser beam, but the resulting degraded beam polarization would not have been troublesome since purity of beam polarization is unimportant in the first instance as will be explained in §3.6. As the laser beam entered the sample, it was important that its E-vector be (at least approximately) perpendicular to the direction in which the scattering was observed in order to be able to collect the isotropic scattering. This requirement is explained in §3.6 below.

3.3.2 The collection optics

When it is remembered that the primary light intensity is overwhelmingly greater than the Raman intensity, it becomes clear that the monochromator should pick up light from the source cylinder only and not, for instance, from any parts of the cell that might reflect unwanted

light into the monochromator slit. The problem of efficiently coupling the source cylinder of the sample to the entrance slit of the monochromator is therefore an important practical matter. Conditions for this optical coupling have been set forth by several authors^{21,22,23}. In our set-up, a 20 cm f.l. collimating lens was used to collect the light scattered from the source region of the sample. This light was then focussed onto the entrance slit of the monochromator by a similar lens, thereby forming an image of unit magnification of the source region. The optical arrangement was set in such a way that the cylindrical scattering volume was parallel to the entrance slit of the monochromator. Since the diameter of the source cylinder was at least 40μ (its diffraction limit) and the slit-width was always kept below 30μ , the entrance slit was therefore always overfilled. In this connection, stronger beam focussing as stated earlier might have been used to increase the signal intensity. Besides, for the same purpose, a larger collection angle might have been used, but this would have caused some loss of polarization definition. Although beam depolarization would not have been a problem as stated previously, a significant increase in the collection angle of the experimental set-up would nevertheless have been limited by the size of the cell windows.

3.4 Monochromator

The spectral composition of the scattered light was analyzed by a one-meter double Czerny-Turner scanning monochromator (Jarell-Ash Model 25-100). This instrument provides the needed discrimination

between the unshifted (primary) and Raman scattered light. It consists of two grating monochromators in tandem and has a diffraction-limited resolution of about 0.3 cm^{-1} . The spectrum of the scattered light is scanned by rotating the gratings about the vertical. The grating advance is controlled by a stepping motor actuating a cosecant-arm mechanical linkage. This results in a grating drive which is linear in wavenumber. An interval of 1 cm^{-1} of the spectrum is scanned when the stepping motor actuates 20 mechanical steps.

Backlash in the mechanical linkage may cause deviations in the linearity of the grating drive. This was particularly noticeable just after reversal of the direction in which the gratings rotate. As a precaution, the grating drive was slewed back well beyond the starting point of the scanning interval and then made to return in slow steps to the starting point in order to take up any backlash before the acquisition of data. However, any discrepancy, owing to backlash, between the indicated wavenumber (as read out by the monochromator) and physical wavenumber did not matter as a fiducial line was included within the range of the scan. This is discussed in §3.8 below.

3.5 Detection and Recording System

The output from the monochromator was focussed onto the photocathode of a photomultiplier tube (RCA C31034). The photomultiplier tube or PMT had a flat spectral sensitivity and a high quantum efficiency which is related to the number of electrons ejected per incident photon. The PMT was used in the photon-counting mode. As in any effective

utilization of the pulse-counting technique, it was necessary to minimize the noise from the PMT. The main type of noise in our experiments was dark noise, that is, the output of the detection system in the absence of any incident radiation. Dark noise arose from the thermal emission of the photocathode. Reduction of dark noise can be achieved by cooling, and therefore, the PMT was enclosed in a refrigerator housing cooled to -40°C . Pulses from the PMT were sent through pulse amplifiers. The amplified pulses were then fed into a discriminator-trigger circuit. The noise pulses in general have a lower pulse-height spectrum than the signal (photo-electron pulses). Following a recommendation of Young²⁴, an optimum discriminator voltage level was set so as to discriminate against pulses of lower height. In the process, the signal intensity was reduced relatively less than the noise and thus, an optimum signal-to-noise ratio was obtained at low light intensities. Each pulse with amplitude greater than the discriminator level was recorded as a photon count.

Pulses designated as photon counts were stored in the memory of a multichannel scalar (MCS). The MCS was part of a Nuclear Data 1200 Analyser system which also comprised a display-oscilloscope and a paper-tape output interface. The channel advance of the MCS was driven synchronously with the grating advance of the monochromator by clock signals derived from a crystal oscillator. Thus, the dispersion of the spectrum recorded in the MCS was governed by the number of grating steps taken during one channel advance. The spectra were therefore recorded linearly in wavenumber. In our experiments, all the spectra were recorded at a

dispersion of $10 \text{ channels/cm}^{-1}$. During acquisition of the spectra, the count rate was displayed on a General Radio 1192B counter-timer.

The signal count rate at the spectral peaks varied from run to run; for the ν_1 line it was between 25 Hz to 75 Hz while for the ν_3 line it ranged between 10 Hz to 25 Hz at the slit-widths used ($<30\mu$). The dark count rate was between 0.6 Hz to 0.8 Hz for the ν_1 runs while for the ν_3 experiments it varied between 0.9 Hz to 1.3 Hz. The higher dark count rate in the case of the ν_3 runs is presumably due to higher ambient temperature, amongst other unknown factors. The dark count rate was measured daily as the Raman spectra were recorded and was subtracted from the spectra before analysis. Each Raman spectrum was recorded over a 13 cm^{-1} interval. The duration of a scan was largely decided by a preliminary survey of the count rate at the spectral peaks prior to the scan. Our aim was to maximize the number of counts in the "peak channel" in order to enhance the S/N ratio without having to scan for an unnecessarily long time. With this view in mind, about two-thirds of the total number of the ν_1 runs lasted for about 3 hrs.each; the remaining ones had a scanning time of about 1.5 hrs.each. In the case of the ν_3 line, given the low signal count rate, it was necessary to scan the spectrum for longer time. Accordingly, almost all the ν_3 scans took about 6 hrs. each. As a routine practice, the dark count rate, the spectral peak count rate, the laser power and room temperature just before and shortly after a scan were checked for consistency. Those scans in which there was severe drifting in any of these variables were suspect, and therefore,

were disregarded in the analysis. Fortunately, such cases were very few.

3.6 Choice of Scattering Geometry

In order to collect the isotropic Raman scattering, the correct scattering or polarization geometry should be used. The way this scattering geometry was selected is described shortly. The light scattered at 90 degrees to the direction of the laser beam may be divided into four basic components. Each may be individually observed in separate experiments. Fig. 3.2 shows the four experimental polarization geometries. Ideally, only the VV geometry permits observation of the isotropic light scattering which is characterized by having its E-vector parallel to the E-vector of the incident light. In other words, the part of the induced molecular dipole moment responsible for VV light scattering is parallel to the incident field. The E-vector of the isotropically scattered light is a scalar times that component of the incident E-vector which is perpendicular to the axis of symmetry of the scattered light. Upon inspection of Fig. 3.2, it becomes evident that the HV, HH and VH polarization geometries do not allow the observation of isotropic light scattering. Only the VV geometry is relevant. Ideal VV light scattering, however, is not achieved in practice. Various factors mentioned earlier like the focussing of the laser beam, depolarizing reflections within the cell and finite collection angle all cause some loss of polarization definition.

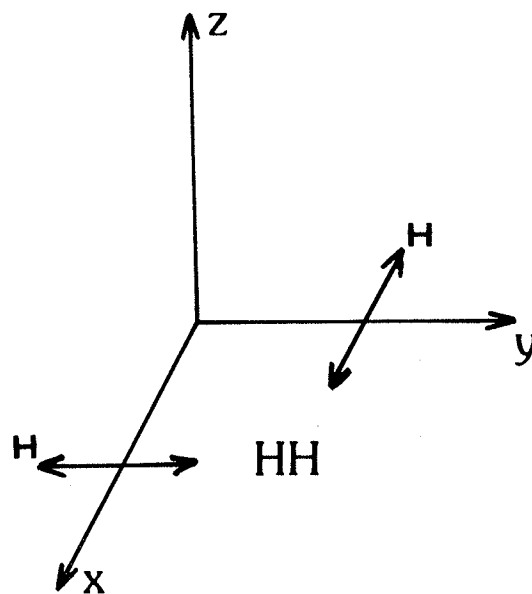
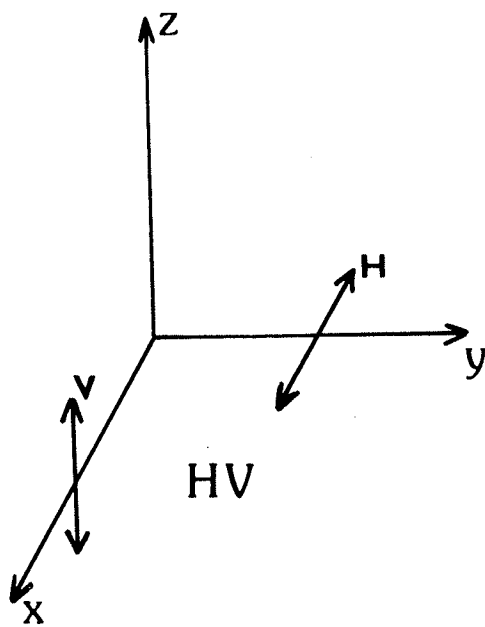
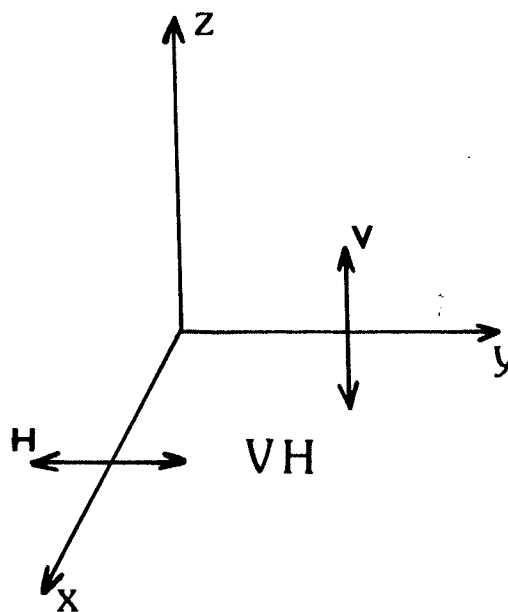
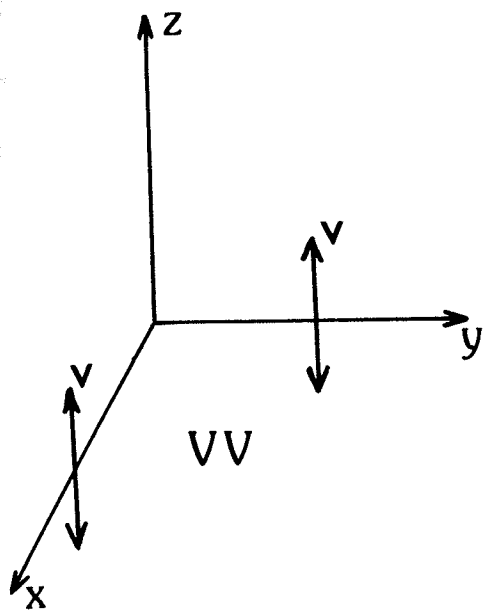
A VV + VH scattering geometry was used for our experiments.

FIG. 3.2

POLARIZATION GEOMETRIES

The incident beam travels in the y-direction and is either vertically (V) or horizontally (H) polarized with respect to the scattering plane.

The scattered light is observed in the x-direction and either the vertically or horizontally polarized component is selected.



This geometry is different from the VV geometry in that no polarization analyzer is required in the collection optics. It should be remarked that a polarization analyzer is needed for the pure VV geometry. The extraneous VH scattering component could have been blocked by a polaroid sheet, but only at the expense of reducing the desired VV signal by half. Such a decrease of the required signal intensity could not be tolerated in the experiments. Besides, the removal of the analyzer did not pose any problem since, even without it, the anisotropic scattering was only about 5% of the measured intensity. Since the intensity of the anisotropic scattering was relatively low and spread out, it would have been very difficult to undertake its measurement in the VH geometry for instance. The measurement in the VV + VH geometry was used as an approximation to the isotropic spectrum; no attempt was made to remove the small anisotropic component by subtraction.

3.7 Measurement of the Slit Function

The "slit function" is the spectral profile of the finite slit-width of the monochromator when the incident light is physically monochromatic. The slit function measures the extent of instrumental distortion or broadening of the Raman spectra. In other words, all information about instrumental distortion of the lineshapes is encoded in the slit function. An analytical correction for the instrumental distortion in the Raman spectra was made. This correction required the slit function of the monochromator. Detailed outlines of the procedure will

be given in Chapter 4.

The slit function in the present work was recorded by scanning over a known emission line of a neon discharge lamp. This measurement was taken at the same slit adjustments as the Raman line in question. That is, each Raman spectrum had its own slit function which was taken shortly before or after the Raman spectrum was recorded. This precaution was taken because it was observed that the slit function could change markedly even at fixed mechanical slit-widths, probably in response to drifts in ambient temperature and humidity. Suitable Ne lines not far removed in frequency from the Raman lines were chosen. In particular, the Ne 19211.1 cm^{-1} line was employed for the slit function measurement for the ν_1 line which was located at 19201.7 cm^{-1} when using the $4880 \text{ \AA}$ excitation line. Likewise, for the ν_3 line at 18263.2 cm^{-1} , the nearest convenient Ne line was at 18516.6 cm^{-1} .

Alternatively, the slit function could have been recorded by scanning over the Rayleigh (unshifted) line of the scattered light. This method was not used for the following reason. On the basis of geometrical optics, the spectral slit-width varies as ν^2 for fixed mechanical slit-width. Using the Rayleigh line would have overestimated the spectral slit-width by as much as 25% and this would have produced a systematic error in the distortion-corrected Raman lineshapes.

3.8 Measurement of Frequency Shifts

It is essential to have an accurate calibration of the frequency

axis for each individual scan in order to be able to discern any frequency shift of the Raman spectrum with changing pressure. As stated in §3.4, the wavenumber indicator on the monochromator could not be relied upon for that purpose. The frequency calibration was achieved by including a fiducial line in each scan. Emission lines from a neon discharge lamp served as useful fiducial lines. In the course of recording a ν_1 spectrum, the 19211.1 cm^{-1} Ne line not only served as an absolute frequency marker, but at the same time was also suitable for the purpose of slit function measurement. This means that no separate runs had to be undertaken in order to obtain the frequency calibration and slit function for any ν_1 spectrum. The experiment was performed as follows. The Ne lamp was switched on at the beginning of the scan. Shortly after the 19211.1 cm^{-1} had been scanned over, the Ne lamp was switched off with the scan continuing uninterrupted.

The case of ν_3 was different. Using the usual 4880 Å excitation line for recording the ν_3 lineshape, no suitable fiducial line was close enough to the ν_3 line so that it could be included in the scanning interval as a frequency marker. The 4880 Å excitation line was therefore used just for obtaining the ν_3 spectrum. For frequency calibration, the 5145 Å excitation line was used because a suitable fiducial line, namely the 17202.7 cm^{-1} Ne line, was close enough to the ν_3 line which occurred at 17206.3 cm^{-1} . It should be noted that the 5145 Å excitation line was used only because it proved to be convenient for frequency calibration. It could not otherwise be used for collecting the ν_3 spectrum to be used in the analysis later as very few counts

were obtained at the slit-widths used in the experiments. At least two frequency calibration runs for the ν_3 spectrum were done at each pressure. In contrast to the case of the ν_1 spectrum, three separate runs were involved for a ν_3 lineshape; one for recording the spectrum, one for the slit function and the last one for an absolute frequency calibration. Details of the pressure shift analysis are given in the following chapter.



CHAPTER 4

DATA ANALYSIS

Measurements of both the linewidth variation and frequency shift of the Raman spectra with increasing pressure will be of central importance when the experimental results are interpreted in terms of the indirect vibrational dephasing theory. This discussion will be considered in Chapter 5. In this chapter, the data reduction problems of the instrumental distortion (or broadening) and frequency shifts of the lineshapes are discussed. The results of the linewidth and frequency shift analysis are given. Two sample spectra are presented so as to illustrate the linewidth analysis. Detailed profiles, however, will be exhibited in the next chapter where they will be compared to theoretical lineshapes.

4.1 Correction for Instrumental Distortion of the Lineshapes

In the experiments, the spectral slit-widths were 0.3 to 0.4 cm^{-1} while the actual measured linewidths were only of the order of 1 cm^{-1} . The spectra therefore suffered considerable instrumental distortion. An attempt is made to correct for this instrumental effect. As the main objective is to study the linewidth trend as a function of pressure, an attempt is made to resolve the linewidth at any single pressure within an error smaller than the variation in linewidth over the contemplated range of pressures. The linewidth will be taken to be the full width at half-maximum (FWHM). The complete lineshape will also be important as will be seen later.

The procedure adopted to correct for the instrumental distortion is to deconvolute the "slit function" out of the measured lineshapes. This method was used by Neuman¹⁴ in earlier work on the Raman Q-branch lineshapes of pure N_2O . In order to gain an insight into the deconvolution process it is helpful to look at the manner in which the instrument distorts a Raman lineshape. This is described in the following.

Consider a perfectly monochromatic beam of light of frequency ν' illuminating the entrance slit of the monochromator. A monochromatic image (with finite width) of the entrance slit will then be formed somewhere in the plane of the exit slit. This image can be made to sweep across the exit slit by adjustment of the grating angle. In the process, the power passing through the exit slit as a function of the indicated wavenumber ν of the monochromator (which depends on grating angle) may be recorded. On account of both the finite width of the entrance slit and the finite width of the exit slit across which the image is swept, the power recorded will be non-zero for a finite range of grating angle. The power spectrum or "bandpass function" recorded will be practically the same function of ν , regardless of the illumination frequency ν' , apart from being bodily displaced along the ν -axis by the amount of any change in ν' . The bandpass function will then be independent of the illumination frequency when recorded as a function of displacement $(\nu - \nu')$ from the illumination frequency. Only the design and adjustment of the mono-

chromator determine the bandpass function which, once suitably normalized (to unit area), is called the slit function $S(v-v')$ of the monochromator. The idea being conveyed here is that an ideal monochromatic "line" is spread out by the monochromator with the result that it has the finite spectral width of the slit function.

Contact is now established between the slit function $S(v-v')$ as defined here and the spectral slit width (SSW) problem alluded to in §3.7. It should be noted that the slit function $S(v-v')$ is independent of the illumination frequency v' only if the amount of change in the illumination frequency is small (e.g. about 10 cm^{-1} or less); for such a case, as stated earlier, the slit function will be basically the same and it will just be bodily displaced along the v -axis. But if the illumination frequency v' is changed by a large amount (say about 1000 cm^{-1}) to a new value, then the slit function recorded as a function of v will be different from the slit function recorded at the original v' . Because the slit function changes, the SSW will change and that change is significant; we recall that the SSW varies as the square of the illumination frequency. This is why as mentioned in §3.7, it is reasonable to use an illumination frequency close to the absolute frequency of the Raman scattered light rather than the Rayleigh line to record the slit function; by so doing no overestimate of the SSW would be made.

Now, consider the illumination of the entrance slit of the monochromator by polychromatic light with spectral intensity distribution

$I(v')$. The power spectrum $I^m(v)$ measured by the instrument may be realized by superposing the instrument response to each of the monochromatic constituents of $I(v')$. For each increment dv' of physical frequency, the instrument response as a function of measured frequency is $dv' I(v') S(v-v')$. By superposing the contributions from such incremental intervals, $I^m(v)$ may be written in the form of a convolution expression:

$$I^m(v) = \int dv' I(v') S(v-v') \quad (4.1)$$

The true spectrum $I(v')$ may be recovered from $I^m(v)$ by solving this integral equation. That is, the aim is to "deconvolute" the kernel $S(v-v')$ out of the convolution.

On a simplistic level, it can be said that the effect of convoluting I with S is just to broaden I^m . Very approximately, the width of the resultant function may be taken to be the sum of the widths of the two convolved functions. Thus, the linewidth of the true function can be estimated by subtracting the width of the slit function from that of the measured profile. However, it should be noted that this relationship is not strictly rigorous and is inaccurate when I and S have widely different widths. It can now be understood why an analytical correction for instrumental distortion has to be made. The linewidth variation over the range of pressure studied is only comparable to the spectral slit-width (SSW) used in the experiments. The SSW is a typical value of the instrumental error in each of the measured linewidths.

Because the instrumental error is similar in magnitude to the pressure-dependent variation that one hopes to discern in the linewidth, the measured spectra by themselves do not directly give a reliable pressure dependence. Hence, some sort of resolution correction must first be made.

4.2 Deconvolution of Measured Lineshapes

A solution of (4.1) may be obtained by using the theory of Fourier transforms. It is well-known that the Fourier transform of the convolution of two functions is given by the product of the transforms of the component functions. The functions which are subjected to Fourier transformation must satisfy certain conditions like being well-defined and absolutely integrable on the whole of the real axis. Such is not the case in the present analysis where discrete spectral data restricted to a finite interval are dealt with. This problem is tackled by replacing integrals with sums and Fourier transforms with finite Fourier series. Then, a relationship formally identical to the convolution theorem is easily obtained provided that the missing values of the spectrum just beyond the edges of the data interval actually vanish. The deconvolution may then be performed and is simple in principle. Essentially, just by dividing the Fourier coefficients of the measured lineshape by the corresponding ones of the slit function one obtains the Fourier coefficients of the true lineshape. Inverse Fourier transformation then restores the true lineshape.

In the practical application of this method, two problems arise. The first problem has to do with the fact that the spectrum generally does not, as stipulated above, vanish beyond the data margins. Normally, the measured intensities inside the data interval are partially dependent on the true intensities just outside, because of the finite width of the slit function. A difficulty thus arises from the impossibility of closing the system of equations relating measured and true intensities. However, upon modification of the data by adding a correction term to those just inside the margins, one finds that the simple form of the convolution theorem can be preserved. This "edge-effect" correction term has to be evaluated from the estimated behaviour of the true spectrum just outside the data margins. In the present analysis, the estimate was obtained by linearly extrapolating the measured spectrum beyond the margins. No serious error would be made either by using the linear approximation or by substituting the measured for true values if the data margins are located in regions of little spectral structure. Care was taken to truncate the data interval at points where the spectrum had fallen almost to background level. Even in the absence of the edge-effect correction term, the deconvoluted lineshapes were affected only near the edges, that is, the uninteresting part of the data interval. In this respect, a more elaborate correction could not be expected to change the linewidth results greatly; any shortcomings of this method were not regarded as a significant source of error.

The second problem is more serious than the first and greatly

limits the quality of the deconvoluted spectra. It is due to the mathematical instability which is inherent in any deconvolution method. Random noise in the data, even in a small amount, produce spurious, rapid oscillations in the deconvoluted profiles^{25,26}. This is a consequence of the high-order Fourier coefficients of the data array (which tend to be dominated by noise) becoming amplified with respect to their low-order (signal-dominated) counterparts during the deconvolution process, when they are divided by corresponding high-order coefficients of the slit function (which tend to be small in relation to low-order coefficients).

In this work, the problem of instability was dealt with by suppressing high-order Fourier coefficients (setting them equal to zero) above a certain cut-off level during reconstruction of the "true" lineshape. The cut-off level was set so that all higher-order components beyond it were rejected while all lower-order components below it were retained. A suitable cut-off was chosen by repeatedly reconstructing the lineshape with higher cut-off levels. Each time, the resultant lineshape was reconvolved with the slit function and compared to the measured spectrum. An acceptable cut-off was the one for which the reduced- χ^2 statistic for the match between the reconvolution and the data was close to unity. Values of χ^2 much greater than unity were taken to indicate systematic error in the reconstruction owing to the excision of Fourier components that made significant contribution to the lineshape trend (as opposed to the undesired oscillations). On the

other hand, values of χ^2 much less than unity indicated that the reconstruction was significantly degraded by noise. However, it should be noted that the cut-off cannot provide a crisp separation between lineshape trend and noise because both have the same Fourier components to some extent. The deconvolution process always entails a compromise between resolution and freedom from oscillations.

Satisfactory results were obtained with the cut-off technique in spite of its shortcomings. It is observed that the deconvoluted spectra exhibit significant resolution enhancement over the data. This is evident from the raised peaks and reduced linewidths of the deconvoluted spectra. Oscillations in the wings of the spectra are also clearly seen. This is attributable to both the measurement process and the nature of the lineshapes themselves. In the first instance, they have been recorded with relatively low signal-to-noise ratio; this promotes oscillations. Secondly, they have sharp structure and therefore can only be accurately restored by the inclusion of relatively high-order Fourier components; the omission of these makes the oscillation problem more acute. Usable deconvoluted lineshapes have nonetheless been obtained at all pressures studied.

Two sample spectra of the ν_1 and ν_3 Q-branches at 3.7 atm are shown in Figs. 4.1 and 4.2 respectively. The measured spectrum (dots) in each figure are shown superimposed on the deconvoluted profile (line); the two are normalized to the same area. It is clear that the deconvoluted profiles show resolution enhancement, as evidenced by

FIG. 4.1

SAMPLE DECONVOLUTION OF ν_1 LINESHAPE

dots: measured ν_1 lineshape

solid line: deconvoluted lineshape

ν_1
3.7 atm

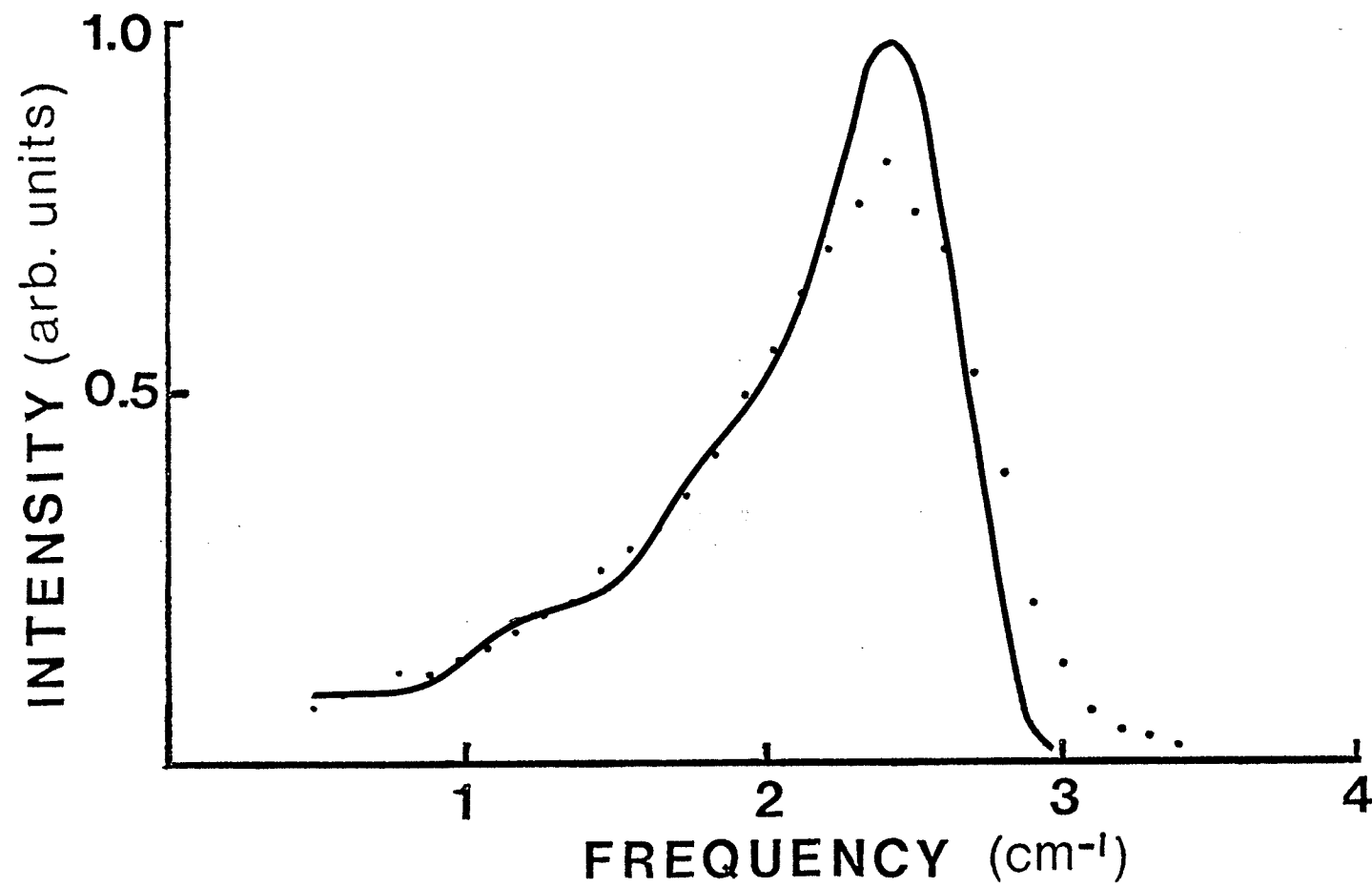


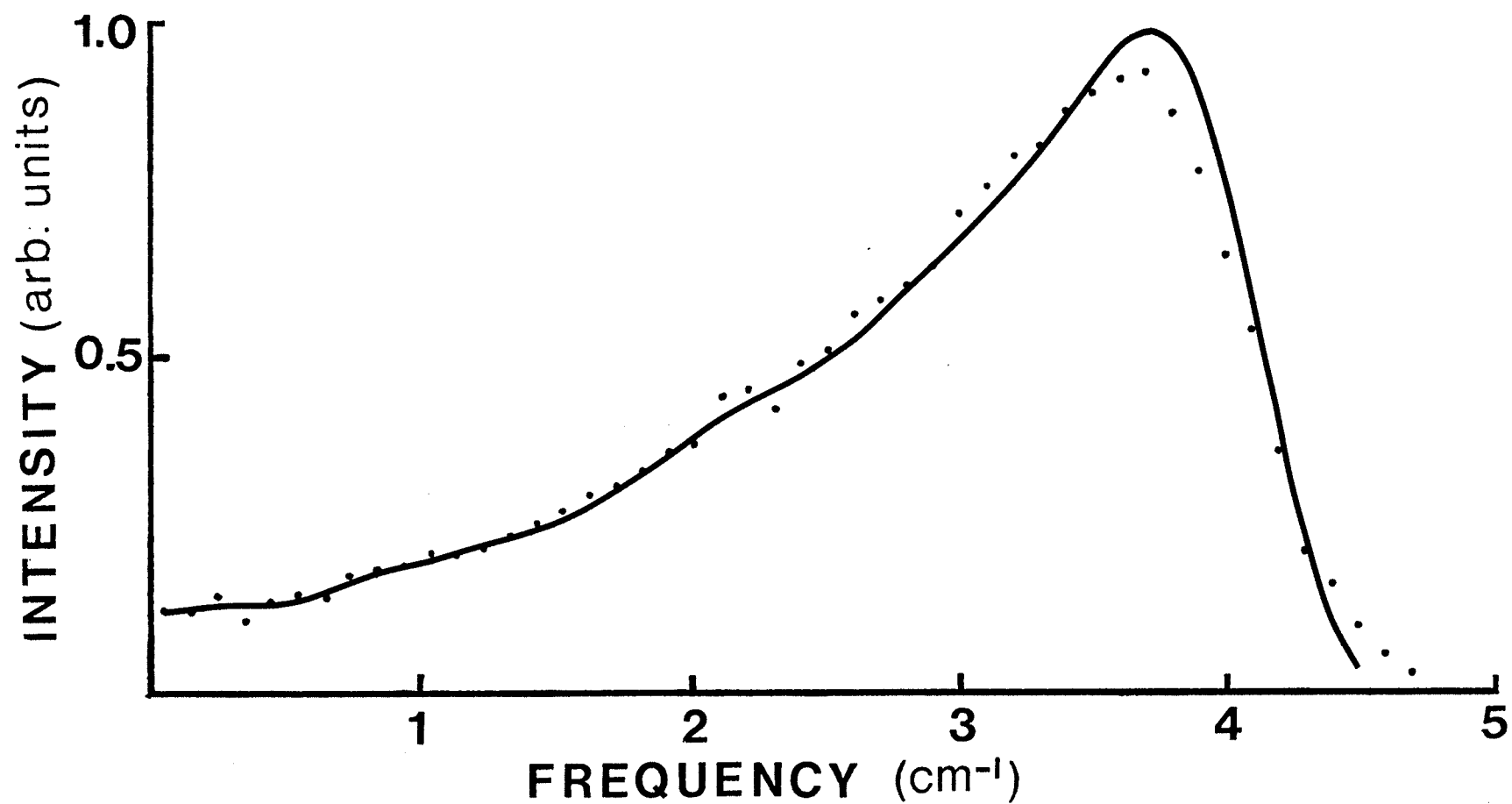
FIG. 4.2

SAMPLE DECONVOLUTION OF ν_3 LINESHAPE

dots: measured ν_3 lineshape

solid line: deconvoluted lineshape

ν_3
3.7 atm



about 13% raise in the peaks and a reduction in linewidths of about 0.2 cm^{-1} . Oscillations in the wings of the deconvoluted spectra are also apparent. Moreover, the deconvoluted profiles display a marked asymmetry which is characteristic at low pressures; this is a consequence of rotation-vibration interaction. The resolution of this asymmetry is important since its disappearance at higher pressures lends support to the indirect-dephasing theory.

4.3 Results of Linewidth Analysis

The resolution-corrected linewidths (FWHM) of the individual spectra for the ν_1 and ν_3 Q-branches are shown in Tables 4.1 and 4.2 respectively. The linewidths were read off from graphs of the deconvoluted lineshapes. Those spectra which had noticeable oscillations were smoothed with French curves before the linewidths were obtained. Because the statistical errors in the original data propagate through the linewidth determination in a very complex manner, an estimate of the "internal" error in a single linewidth value has not been made. Alternatively, an error estimate based on the spread among individual linewidths at a given pressure is possible. In Tables 4.1 and 4.2, the error estimate in the average linewidth at a given pressure is just the average deviation from the mean linewidth. The theoretical linewidths derived from the theoretical lineshapes are also given in Tables 4.1 and 4.2.

4.4 Frequency Shift Analysis

It was stated in Chapter 1 and shown in §2.7 that the indirect vibrational dephasing theory predicts that, with large increase in

TABLE 4.1
DECONVOLUTED ν_1 Q-BRANCH LINEWIDTHS AT 294 K

System	Experimental		Theoretical FWHM (cm^{-1})
	FWHM (cm^{-1})	Average FWHM (cm^{-1})	
N_2O (1.7 atm)	0.75	0.80 ± 0.04	0.80
	0.80		
	0.86		
N_2O (1.7 atm) + ^2Ar (2.0 atm)	0.73	0.70 ± 0.07	0.83
	0.78		
	0.73		
	0.56		
N_2O (1.7 atm) + ^2Ar (6.1 atm)	0.79	0.65 ± 0.09	0.79
	0.69		
	0.48		
	0.63		
N_2O (1.7 atm) + ^2Ar (9.8 atm)	0.54	0.61 ± 0.07	0.73
	0.60		
	0.69		
	0.53		
	0.70		
N_2O (1.7 atm) + ^2Ar (18.4 atm)	0.52	0.55 ± 0.06	0.61
	0.64		
	0.49		
N_2O (1.7 atm) + ^2Ar (36.7 atm)	0.61	0.52 ± 0.07	0.45
	0.55		
	0.47		
	0.43		
N_2O (1.7 atm) + ^2Ar (79.2 atm)	0.36	0.43 ± 0.06	0.28
	0.38		
	0.53		
	0.45		
N_2O (1.7 atm) + ^2Ar (142.5 atm)	0.30	0.37 ± 0.07	0.17
	0.48		
	0.27		
	0.40		
	0.32		
	0.45		

TABLE 4.2
DECONVOLUTED ν_3 Q-BRANCH LINEWIDTHS AT 296 K

System	Experimental		Theoretical FWHM (cm^{-1})
	FWHM (cm^{-1})	Average FWHM (cm^{-1})	
N_2O (2.4 atm)	1.55 1.51 1.49	1.52 ± 0.02	1.55
N_2O (2.4 atm) + ^2Ar (1.3 atm)	1.43 1.65 1.58 1.54	1.55 ± 0.07	1.63
N_2O (2.4 atm) + ^2Ar (5.9 atm)	1.58 1.54 1.48 1.60	1.55 ± 0.04	1.68
N_2O (2.4 atm) + ^2Ar (9.5 atm)	1.49 1.59 1.45 1.75	1.57 ± 0.10	1.65
N_2O (2.4 atm) + ^2Ar (16.3 atm)	1.40 1.40 1.33	1.38 ± 0.03	1.55
N_2O (2.4 atm) + ^2Ar (37.4 atm)	1.06 1.34 1.28 0.85 1.20	1.15 ± 0.15	1.26
N_2O (5 atm) + ^2Ar (72.2 atm)	1.10 1.18 1.05 1.03	1.09 ± 0.05	0.94
N_2O (2.4 atm) + ^2Ar (76.9 atm)	0.75 0.85 1.05	0.88 ± 0.11	0.91
N_2O (5 atm) + ^2Ar (135.5 atm)	0.48 0.80 0.73 0.94 0.81	0.75 ± 0.12	0.61

the relaxation rate, the frequency of the peak of a Raman spectrum gets shifted and eventually coincides with the ensemble averaged frequency of the oscillators, that is, the central frequency ω_0 . This is what is implied when it is said that the spectrum collapses about its central frequency at higher pressures. An attempt has been made to measure the frequency shifts of the peaks of the Raman spectra. Details of the experimental method were described in §3.8. Here, the analysis and results of the experimental measurements are given. For convenience in the discussion at a later stage, the theoretical results derived from the theoretical lineshapes are also presented. The detailed derivation of the theoretical lineshapes themselves will be described in the next chapter.

The pressure-dependent frequency shift of a Raman spectrum is conventionally defined as the frequency difference of the peak of the spectrum at a higher pressure with respect to a reference point. In this work, the peak frequency shift of the deconvoluted spectrum is given relative to the frequency of $Q(0)$. $Q(0)$ is the frequency of the vibrational mode when rotation-vibration interaction is not taken into consideration. It has been chosen as a reference frequency because its value is very well defined. The frequencies of $Q(0)$ in vacuo are 1285.0 cm^{-1} and 2223.5 cm^{-1} for the ν_1 and ν_3 vibrational modes respectively²⁸. Since only the vacuum values of the $Q(0)$ frequencies are accurately known, accordingly the vacuum frequencies of the laser (excitation) and Ne lines are used in all calculations. In fact, all frequencies quoted in this thesis are vacuum values.

4.4.1 Peak frequency shifts of the ν_1 lineshapes

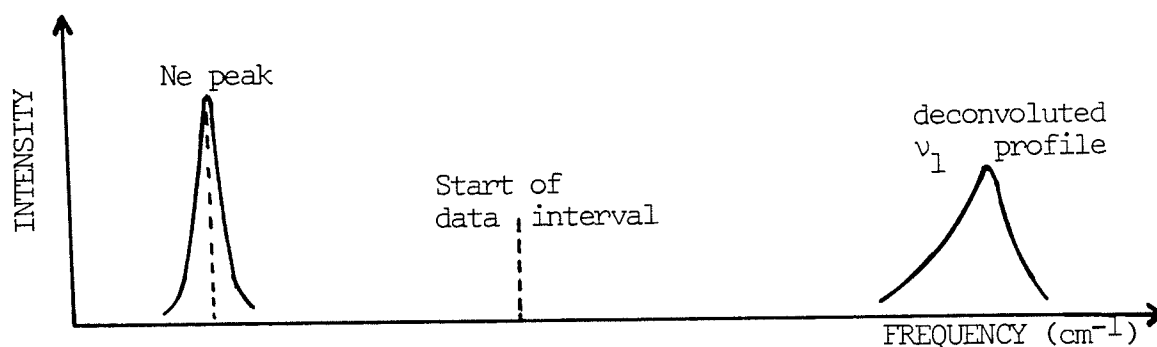


FIG. 4.3 SCHEMATIC ILLUSTRATION OF ν_1 FREQUENCY SHIFT ANALYSIS

Figure 4.3 illustrates the procedure for obtaining the peak frequencies of the deconvoluted ν_1 spectra. The sequential steps are as follows:

- (i) The position of the Ne line relative to the laser line is found by taking the difference between the laser frequency (20486.7 cm^{-1}) and Ne line frequency (19211.1 cm^{-1}). This is 1275.6 cm^{-1} .
- (ii) The number of channels between the Ne spectral peak and the starting point of the data interval is found.
- (iii) The number of channels from the starting point of the data interval to the deconvoluted ν_1 peak is added to the result in (ii).
- (iv) The result in (iii) is multiplied by 0.1 cm^{-1} and added to

1275.6 cm^{-1} . This gives the frequency shift (i.e. the Raman shift) of the ν_1 peak relative to the laser line. The results are shown in Table 4.3. For comparison, the Raman shifts of the peaks of the theoretical lineshapes are also presented in Table 4.3

We can now obtain the average peak frequency shifts relative to the reference frequency stated earlier. Tables 4.4 shows the experimental peak shifts relative to the frequency of $Q(0)$; the corresponding theoretical peak shifts are also given. The error estimate in the average shift at a given pressure is just the average deviation from the mean.

4.4.2 Peak-frequency shifts of the ν_3 lineshapes

For reasons already mentioned in §3.8, a different approach was necessary in order to determine the pressure-dependent peak shifts of the ν_3 lineshapes. The ideas underlying the procedure adopted are displayed in Fig. 4.4. A very useful criterion in the frequency shift analysis here is that the deconvolution process preserves the magnitude of the frequency separation Δ between the centroid of the measured ν_3 lineshape and the centroid of the fiducial Ne spectral profile (see Appendix). This fact is displayed in Fig. 4.4(c) and 4.4(d); in particular, Fig. 4.4(c) illustrates the pressure shift measurement described in §3.8. The hypothetical deconvolution of Fig. 4.4(c) is exhibited in Fig. 4.4(d); from the manner of implementing the deconvolution program, the deconvolution of the Ne spectral profile would

TABLE 4.3

RAMAN SHIFTS OF PEAKS OF DECONVOLUTED ν_1 LINESHAPES

System	Experimental		Theoretical Shift (cm^{-1})
	Shift (cm^{-1})	Average Shift (cm^{-1})	
N_2O (1.7 atm)	1284.3	1284.5 ± 0.13	1284.83
	1284.7		
	1284.5		
N_2O (1.7 atm) + ^2Ar (2.0 atm)	1284.4	1284.6 ± 0.10	1284.70
	1284.5		
	1284.8		
	1284.6		
N_2O (1.7 atm) + ^2Ar (6.1 atm)	1284.5	1284.5 ± 0.03	1284.58
	1284.5		
	1284.6		
	1284.5		
N_2O (1.7 atm) + ^2Ar (9.8 atm)	1284.5	1284.4 ± 0.10	1284.48
	1284.2		
	1284.6		
	1284.4		
	1284.4		
N_2O (1.7 atm) + ^2Ar (18.4 atm)	1284.4	1284.4 ± 0.03	1284.38
	1284.4		
	1284.3		
N_2O (1.7 atm) + ^2Ar (36.7 atm)	1284.4	1284.3 ± 0.10	1284.28
	1284.2		
	1284.2		
	1284.2		
N_2O (1.7 atm) + ^2Ar (79.2 atm)	1283.9	1284.0 ± 0.10	1284.20
	1284.1		
	1284.1		
	1283.9		
N_2O (1.7 atm) + ^2Ar (142.5 atm)	1283.8	1283.8 ± 0.10	1284.18
	1283.8		
	1283.9		
	1283.8		
	1284.0		
	1283.7		

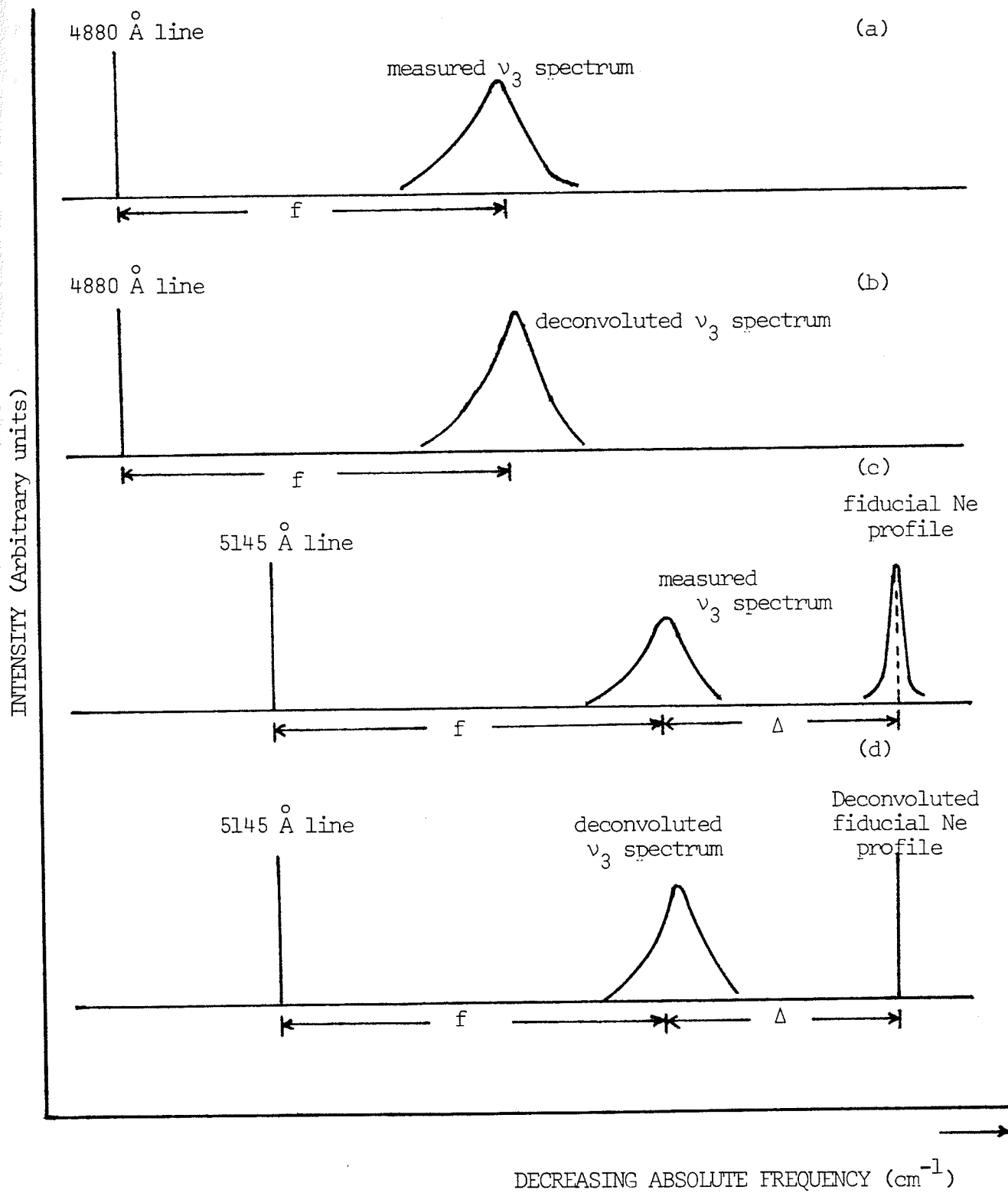
TABLE 4.4

AVERAGE PEAK FREQUENCY SHIFTS OF DECONVOLUTED ν_1
 LINESHAPES RELATIVE TO FREQUENCY OF Q(0)

System	Shift (cm^{-1})	
	Experimental	Theoretical
N_2O (1.7 atm)	-0.5 ± 0.13	-0.17
N_2O (1.7 atm) + ^2Ar (2.0 atm)	-0.4 ± 0.10	-0.30
N_2O (1.7 atm) + ^2Ar (6.1 atm)	-0.5 ± 0.03	-0.42
N_2O (1.7 atm) + ^2Ar (18.4 atm)	-0.6 ± 0.10	-0.52
N_2O (1.7 atm) + ^2Ar (18.4 atm)	-0.6 ± 0.03	-0.62
N_2O (1.7 atm) + ^2Ar (36.7 atm)	-0.7 ± 0.10	-0.72
N_2O (1.7 atm) + ^2Ar (79.2 atm)	-1.0 ± 0.10	-0.80
N_2O (1.7 atm) + ^2Ar (142.5 atm)	-1.2 ± 0.10	-0.82

FIG. 4.4

SCHEMATIC ILLUSTRATION OF ν_3 FREQUENCY SHIFT ANALYSIS



produce a spike at the position of the measured peak of the Ne spectrum in the data record. This spike may be assigned the tabular absolute frequency, namely 17202.7 cm^{-1} , of the Ne fiducial line.

Now, the measured ν_3 spectrum of primary interest in the lineshape analysis is shown schematically in Fig. 4.4(a). Its deconvolution is displayed in Fig. 4.4(b). In view of the fact that Δ is invariant under deconvolution, the absolute frequency of the centroid of the deconvoluted ν_3 spectrum must lie a frequency Δ beyond the tabular value of the Ne line frequency, that is, the centroid of the deconvoluted Ne line. Thus, once Δ is calculated from the centroids of the measured profiles, the absolute frequency of the centroid of the deconvoluted or true ν_3 spectrum is known and its Raman shift relative to the excitation line may be readily obtained from the relation:

$$\begin{aligned} f &= [(\text{Excitation frequency}) - (\text{Ne line frequency}) - \Delta] \\ &= [19429.8 - 17202.7 - \Delta] \\ &= [2227.1 - \Delta] \text{ cm}^{-1} \end{aligned}$$

A known Raman shift value f may thus be assigned to a known position (the centroid) on the deconvoluted lineshape, furnishing a reference point on the frequency axis. The peak frequency for each spectrum may then be accurately located by reference to the known centroid frequency.

Table 4.5 shows the peak frequency shifts of the deconvoluted ν_3 lineshapes relative to the excitation line (i.e. the Raman shifts). As for the case of ν_1 , the peak frequency shifts relative to the reference frequency may now be written down. Table 4.6 presents the peak frequency shifts relative to the frequency of $Q(0)$; the corresponding theoretical peak shifts are also given. The error estimate quoted in the average shift at a given pressure is the average deviation from the mean.

TABLE 4.5

RAMAN SHIFTS OF PEAKS OF DECONVOLUTED ν_3 LINESHAPES

System	Experimental		Theoretical Shift (cm^{-1})
	Shift (cm^{-1})	Average Shift (cm^{-1})	
N_2O (2.4 atm)	2223.40	2223.42 ± 0.06	2223.24
	2223.50		
	2223.36		
N_2O (2.4 atm) + ^2Ar (1.3 atm)	2223.28	2223.28 ± 0.02	2223.10
	2223.30		
	2223.29		
	2223.25		
N_2O (2.4 atm) + ^2Ar (5.9 atm)	-	-	2222.85
N_2O (2.4 atm) + ^2Ar (9.5 atm)	2223.04	2223.03 ± 0.04	2222.70
	2223.02		
	2222.96		
	2223.10		
N_2O (2.4 atm) + ^2Ar (16.3 atm)	2222.86	2222.81 ± 0.03	2222.55
	2222.79		
	2222.78		
N_2O (2.4 atm) + ^2Ar (37.4 atm)	2222.45	2222.51 ± 0.03	2222.25
	2222.51		
	2222.54		
	2222.56		
	2222.51		
N_2O (5 atm) + ^2Ar (72.2 atm)	2222.08	2222.02 ± 0.06	2222.00
	2221.91		
	2222.01		
	2222.06		
N_2O (2.4 atm) + ^2Ar (76.9 atm)	2222.01	2222.00 ± 0.01	2222.00
	2222.01		
	2221.99		
N_2O (5 atm) + ^2Ar (135.5 atm)	2221.66	2221.73 ± 0.04	2221.90
	2221.77		
	2221.72		
	2221.72		
	2221.78		

TABLE 4.6
 AVERAGE PEAK FREQUENCY SHIFTS OF DECONVOLUTED ν_3
 LINESHAPES RELATIVE TO FREQUENCY OF Q(0)

System	Shift (cm^{-1})	
	Experimental	Theoretical
N_2O (2.4 atm)	-0.08 ± 0.06	-0.26
N_2O (2.4 atm) + ^2Ar (1.3 atm)	-0.22 ± 0.02	-0.40
N_2O (2.4 atm) + ^2Ar (5.9 atm)	-	-0.65
N_2O (2.4 atm) + ^2Ar (9.5 atm)	-0.47 ± 0.04	-0.80
N_2O (2.4 atm) + ^2Ar (16.3 atm)	-0.69 ± 0.03	-0.95
N_2O (2.4 atm) + ^2Ar (37.4 atm)	-0.99 ± 0.03	-1.25
N_2O (5 atm) + ^2Ar (72.2 atm)	-1.48 ± 0.06	-1.5
N_2O (2.4 atm) + ^2Ar (76.9 atm)	-1.50 ± 0.01	-1.5
N_2O (5 atm) + ^2Ar (135.5 atm)	-1.77 ± 0.04	-1.6

CHAPTER 5

DISCUSSION

In this chapter, the experimental findings are interpreted in terms of the indirect-dephasing theory elaborated in Chapter 2. On the basis of this theory, theoretical lineshapes of the Q-branches are generated and compared to their experimental counterparts.

5.1 Possible Line-broadening Mechanisms

Here, we consider briefly the possible line-broadening mechanisms that may be advanced to account for the lineshape behaviour. Our aim is to identify the mechanisms that feature prominently in our measured lineshapes. Line-broadening mechanisms may be conveniently classified into two groups: Homogeneous and inhomogeneous mechanisms.

The first and most fundamental cause of homogeneous broadening is natural or radiative broadening due to spontaneous decay of an excited state. This effect is negligible in our experiments. Homogeneous broadening may also arise either from inelastic interactions which redistribute energy from the vibrational mode in question among other degrees of freedom or from quasi-elastic interactions which cause random fluctuations of the vibrational phase without inducing changes in quantum number of the vibrational mode in question. The former processes are labelled "energy decay" or "depopulation" processes, examples of which are collision-induced vibration-to-translation (V-T) and vibration-to-vibration (V-V) energy transfer processes. Under our experimental conditions, V-T energy transfer does

not produce significant broadening in the lineshapes. V-V energy relaxation may also be discounted because of the absence of any near-resonance energy decay scheme. We may therefore discount energy relaxation of either vibrational mode. The only homogeneous broadening mechanisms that have to be considered are dephasing mechanisms.

Inhomogeneous broadening may be attributable to the Doppler effect which is essentially a form of intermolecular coupling between velocity and vibrational frequency of the selfsame molecule. However, Doppler broadening is not significant in the experimental lineshapes. Moreover, various sorts of intramolecular coupling may give rise to inhomogeneous broadening. For instance, the coupling of the vibrational mode of interest with other modes may appear as a hot-band structure superimposed on the main spectral profile. A hot-band of considerable intensity owing to the sizable population of the (0 1 0) level is in fact present near each of the ν_1 and ν_3 fundamental modes. These hot-bands are of no consequence, however, because their Q-branches do not overlap with the main lineshape and their O- and S- branches contribute only a weak featureless background.

The only remaining intramolecular mechanism that might affect the lineshape behaviour is rotation-vibration (RV) interaction. This will be discussed below. In general, intermolecular coupling is expected to give rise only to homogeneous broadening, on account of the speed with which intermolecular variables relax in the gas phase. It then follows that RV coupling may be taken to be the only source of

inhomogeneous broadening. Thus far, the mechanisms that affect the lineshapes may be restricted to homogeneous dephasing and inhomogeneous RV coupling.

We find that inhomogeneous RV broadening actually accounts for the observed low-density spectral profiles. However, the observed symmetrisation, or indeed any change of the lineshapes, with increasing density cannot be explained by the RV coupling. Some form of dephasing must therefore be at least partially responsible for the spectra at higher densities. At this point, there are two possibilities. One is that the RV broadening remains inhomogeneous with increasing density; this is what we would expect if collisions are quite ineffective in inducing rotational transitions. This precludes the "indirect-dephasing" mechanism described in Chapter 2. The dephasing would then be direct, that is, the direct result of fluctuation in the intermolecular variables. In this regard, it would not depend on intramolecular coupling and the lineshape would be a convolution of the fixed RV (free-molecule) profile with the density-dependent lineshape arising from the dephasing alone. This convolution would produce a profile which cannot be much different, in particular, it cannot be markedly more symmetric than the RV profile itself, unless the other (dephasing) profile is at least comparable in width. But then the convolution would be considerably broader than the RV profile alone. This contradicts our experimental findings that both for ν_1 and ν_3 , the lineshapes become almost completely symmetric with rising density. Therefore, a purely direct dephasing mechanism is discounted.

The other option is that the RV coupling itself changes into a homogeneous dephasing mechanism as rotational transitions become more frequent with increasing density. This is the indirect-dephasing theory discussed in Chapter 2. From the contradiction encountered above when purely direct dephasing was assumed, we assert that the actual dephasing must be indirect. If this is valid, then we find that a single coupling mechanism (RV) is responsible for all the lineshape behaviour; in fact this same mechanism was identified to be prominent in the Q-branch spectra of pure N_2O gas^{14,15}. We may therefore apply the lineshape formalism (2.11) of §2.6 at all densities. We shall use this to analyze the N_2O Q-branch spectra perturbed by argon.

5.2 Lineshape Analysis

Having identified the prominent mechanism for vibrational relaxation in our experiments, we now proceed to apply the indirect-dephasing theory to account for the Q-branch lineshapes.

5.2.1 Generation of theoretical lineshapes

The working expression for the lineshape $I(\omega)$ is (2.11) of Chapter 2:

$$I(\omega) \propto \vec{f} \cdot \text{Re}\{[i(\omega - \omega_0) \tilde{E} - \tilde{\Omega} + \tilde{D}]^{-1}\} \cdot \vec{e} \quad (2.11)$$

We start by generating the matrix $\tilde{\Omega}$ in (2.11). The Q-branch frequencies

for the fundamental vibrational transitions of a linear molecule are given by

$$Q(J) = Q(0) - \alpha_K J(J+1) \quad (5.1)$$

This expression differs from that for a diatomic molecule insofar as the RV interaction constant α_K is specific to the vibrational mode ν_K in question. For the N_2O molecule²⁹, we have

$$\alpha_1 = 1.72 \times 10^{-3} \text{ cm}^{-1} \text{ and } \alpha_3 = 3.47 \times 10^{-3} \text{ cm}^{-1}.$$

Redefining ω_0 as the band origin $Q(0)$ rather than as the thermal average frequency, the matrix $\tilde{\Omega}$ may be written in the form

$$\tilde{\Omega} = \alpha_K \begin{bmatrix} 0 & & & & & \\ & -1 \times 2 & & & & \\ & & -2 \times 3 & & & \\ & & & -3 \times 4 & & \\ & & & & \ddots & \\ & & & & & \ddots \end{bmatrix} \quad (5.2)$$

It should be noted that the shift in ω_0 does not affect the theoretical lineshape (2.11) so long as we retain the convention that the j^{th} resonance frequency is $\omega_0 + \omega_j$, and alter the ω_j and $\tilde{\Omega}$

accordingly as has been done in (5.2).

For a linear molecule, the thermal weight vector $\vec{f}$ satisfies the relation

$$f(J) \propto (2J+1)\exp(-hB_0 J(J+1)/KT) \quad (5.3)$$

where B_0 is the rotational constant.

For N_2O ,

$$B_0 = 0.41901 \text{ cm}^{-1}.^{29}$$

In the analysis, all J-levels with populations $\geq 1\%$ of that of the most probable level are used. This entails the inclusion of all levels with J-values from 0 to 54. The weights $f(0)$ to $f(54)$ are calculated using (5.3) and then normalised so that they sum to unity. The corresponding 55-square D-matrix may then be constructed in accordance with the J-scrambling model by the use of equation (2.5). Only the relaxation rate r must now be specified before the lineshapes may be calculated from (2.11).

From (5.2), it is clear that the calculations for ν_1 and ν_3 differ only in the value of α_K multiplying the matrix $\tilde{\Omega}$. The stochastic matrix $\tilde{D}$ is the same for either vibrational mode. It has to do only with rotational relaxation and provides no vibrational information. In this regard, all information about rotational relaxation obtained by studying either spectral line must be the same.

5.2.2 Calibration of relaxation rate versus density

As stated in §2.5, we choose to associate a relaxation rate r with each experimental density and then proceed to generate the corresponding theoretical lineshape. For our case of N_2O -Argon mixtures, the overall relaxation rate r follows from (2.6):

$$r = C_1 n_1 + C_2 n_2, \quad (5.4)$$

where

C_1 = ratio of relaxation rate (owing to N_2O - N_2O collisions) to density of N_2O molecules,

n_1 = density of N_2O molecules,

C_2 = ratio of relaxation rate (owing to N_2O -Ar collisions) to density of Ar atoms,

and n_2 = density of Ar atoms.

Equation (5.4) contains the fact that the relaxation of the Q-branches arises from N_2O - N_2O collisions as well as from N_2O -Ar collisions, with the latter obviously being more and more predominant with rising density of Ar atoms. From (5.4), we have

$$b = (r - C_1 n_1) = C_2 n_2, \quad (5.5)$$

from which $b:n_2 = C_2 = \text{constant}$.

The ratio $b:n_2$ is just the ratio of the relaxation rate (owing to N_2 -Ar collisions) to the density of Ar atoms, and it is fixed if we assume that the relaxation is caused by binary collisions. This ratio cannot be obtained by direct means and therefore, we resort to an empirical calibration method. From (5.5), we can write

$$\log b = \log C_2 + \log n_2, \quad (5.6)$$

where C_2 is the constant ratio $b:n_2$. Because of the constant difference between $\log b$ and $\log n_2$, we can use a graphic technique (displayed in Fig. 5.1) to determine the quantity C_2 .

The theoretical lineshape, and in particular its width, should represent the same function of b as the experimental lineshape does of n_2 , the density of perturbers (Ar atoms). If C_2 is constant, then a plot of the log of theoretical linewidth versus $\log b$ should appear the same as a plot of the log of experimental linewidth versus $\log n_2$, except bodily displaced from it by $\log C_2$ along the abscissa. One can obtain a best estimate of $\log C_2$ by superimposing one graph on the other and sliding it horizontally across the latter until the two are most nearly in coincidence. The extent of the shift along the abscissa required to "match" the two graphs gives an estimate of $\log C_2$. The best match between the two

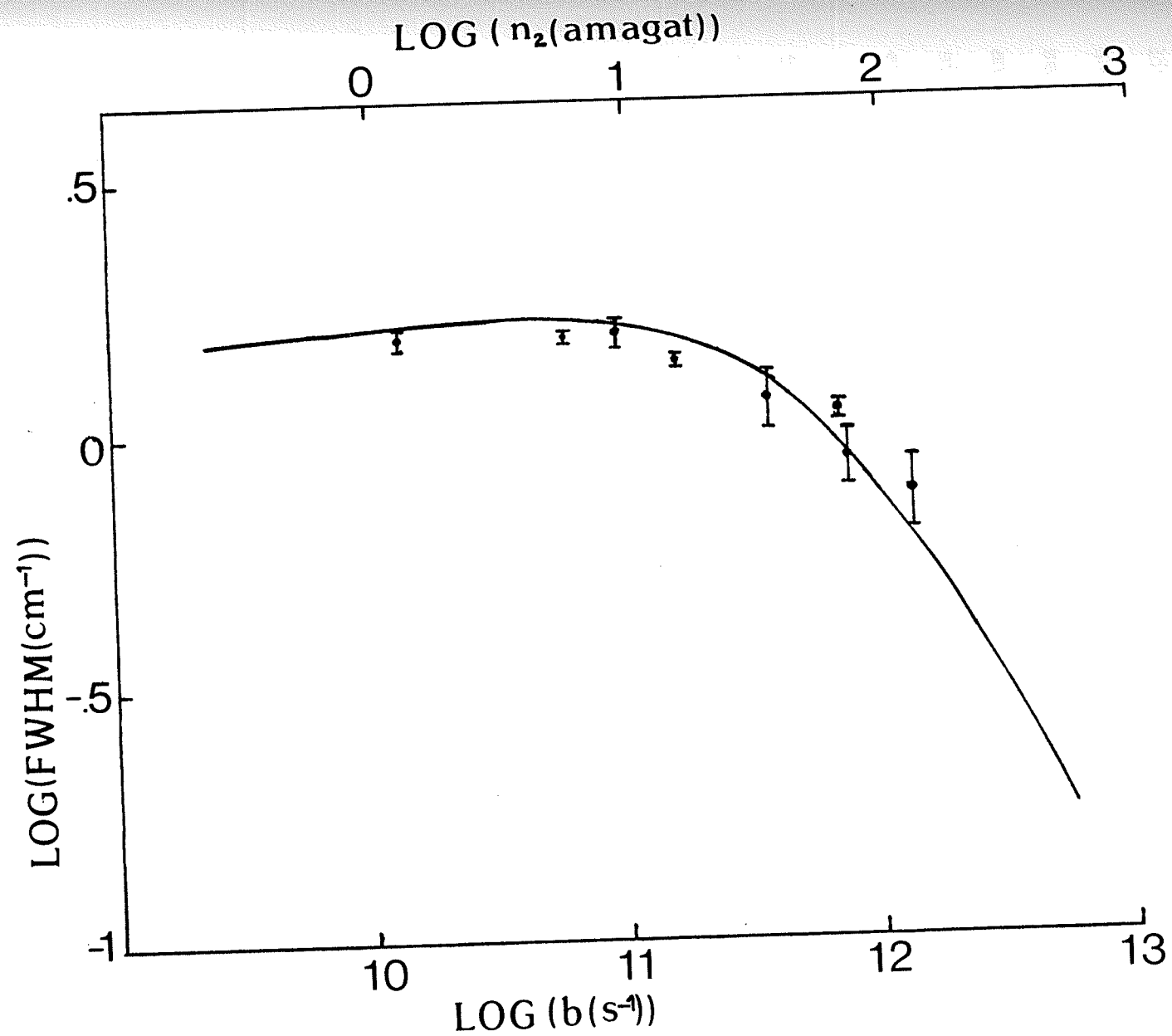
FIG. 5.1

COMPARISON OF THEORETICAL AND EXPERIMENTAL
LINEWIDTH TRENDS - ν_3

solid line: logarithm of theoretical linewidth as function of
logarithm of relaxation rate b

dots: logarithm of average experimental linewidth data,
plotted against logarithm of argon density n_2

The two horizontal scales are displaced so as to produce the best
agreement between the two trend lines.



graphs was decided by a least-squares fit method.

In the following, we describe how we have obtained the theoretical linewidth trend appearing in Fig. 5.1. The theoretical linewidth trend has been obtained from the inspection of the line-shapes generated from (2.11). These have been calculated for a series of r -values falling at roughly uniform logarithmic intervals, and spanning the range of plausible values, that is, values similar to the kinetic-theory collision rates appropriate to our experiments.

In this work, we have chosen to study the linewidth, rather than some other lineshape parameter, because it is readily obtained from mere examination of the lineshape, without detailed calculation or knowledge of the analytical form of the profile. The linewidth is particularly a suitable criterion for comparing profiles of differing or unknown analytical form. Moreover, the narrowing phenomenon at high density is assessed through the linewidth of the spectral profile and therefore, it is of basic physical significance.

Using the graphic technique described earlier, the theoretical linewidth trend for ν_3 is related to the experimental trend. Fig. 5.1 illustrates the two trends superimposed to produce the best match between them, so that matching values on the b - and n_2 - scales lie one atop the other. The experimental linewidth data are those of Table 4.2. The density at all pressures was calculated using the ideal gas law since any correction based on PVT data³⁰ made practically no difference to the calculations. Fig. 5.1 displays clear

agreement between experimental and theoretical linewidth trends over the whole range of densities studied. The predicted motional narrowing is clearly evident in the experimental linewidth trend. The theoretical linewidth trend shows the asymptotic linearity with increasing relaxation rate b or with increasing density of perturber (argon) atoms as first stated in Chapter 1.

The least-squares fit method for the best match between the two trends gives a value of

$$\log C_2 = 0.04 \pm 0.03,$$

from which

$$C_2 = b:n_2 = 1.1 \pm 0.1 \times 10^{10} \text{ S}^{-1}/\text{amagat}$$

This value of C_2 may now be inserted in equation (5.4) in order to find r . The quantities n_1 and n_2 are known experimental densities while C_1 is also a known quantity. It was evaluated in earlier work on motional narrowing in pure N_2O gas¹⁴. Its value is $6.7 \times 10^9 \text{ S}^{-1}/\text{amagat}$. Thus, the overall relaxation rate r for each experimental density of the mixtures may be calculated once C_2 is known.

5.2.3 Comparison between theory and experiment - ν_3 Q-branch

Once a value of r is assigned to a particular experimental

density, the corresponding theoretical lineshape may be calculated using (2.11). The theoretical lineshapes for ν_3 are shown superimposed on their deconvoluted experimental counterparts in Fig. 5.2. The two profiles have been normalized to the same peak height in each case. The frequency origins are arbitrary. Although an absolute frequency calibration was included in the experimental measurements, for the sake of convenience and ease in comparison, the experimental profiles have been arbitrarily positioned so that their peaks coincide with the theoretical peaks in Fig. 5.2. The experimental profile chosen for display at a particular pressure is the one whose linewidth is closest to that of the theoretical lineshape.

From Table 4.2 and Fig. 5.2, we find that convincing agreement is obtained at all but the highest density. Progressive narrowing and symmetrisation of the profiles with increasing density are observed. This behaviour is specific to the indirect-dephasing theory; it cannot be explained by the usual collision broadening process whereby appreciable symmetrisation could only occur along with an increase in linewidth at least comparable to the original width of the lineshape. So, as far as direct dephasing is concerned, its effect is seen to have been almost eliminated by using argon atoms as perturbers. In brief, the proposed indirect dephasing mechanism succeeds quite well in accounting for the lineshapes at densities up to 73.1 amagat. The particular scheme of rotational relaxation, namely the J-scrambling model, also agrees with experimental results; since the lineshapes are model-dependent an accurate prediction of the detailed lineshapes provides confirmation

FIG. 5.2

COMPARISON OF THEORETICAL AND EXPERIMENTAL
LINESHAPES - ν_3

Except for (a), the specified density is that of the N_2O -Ar mixture.

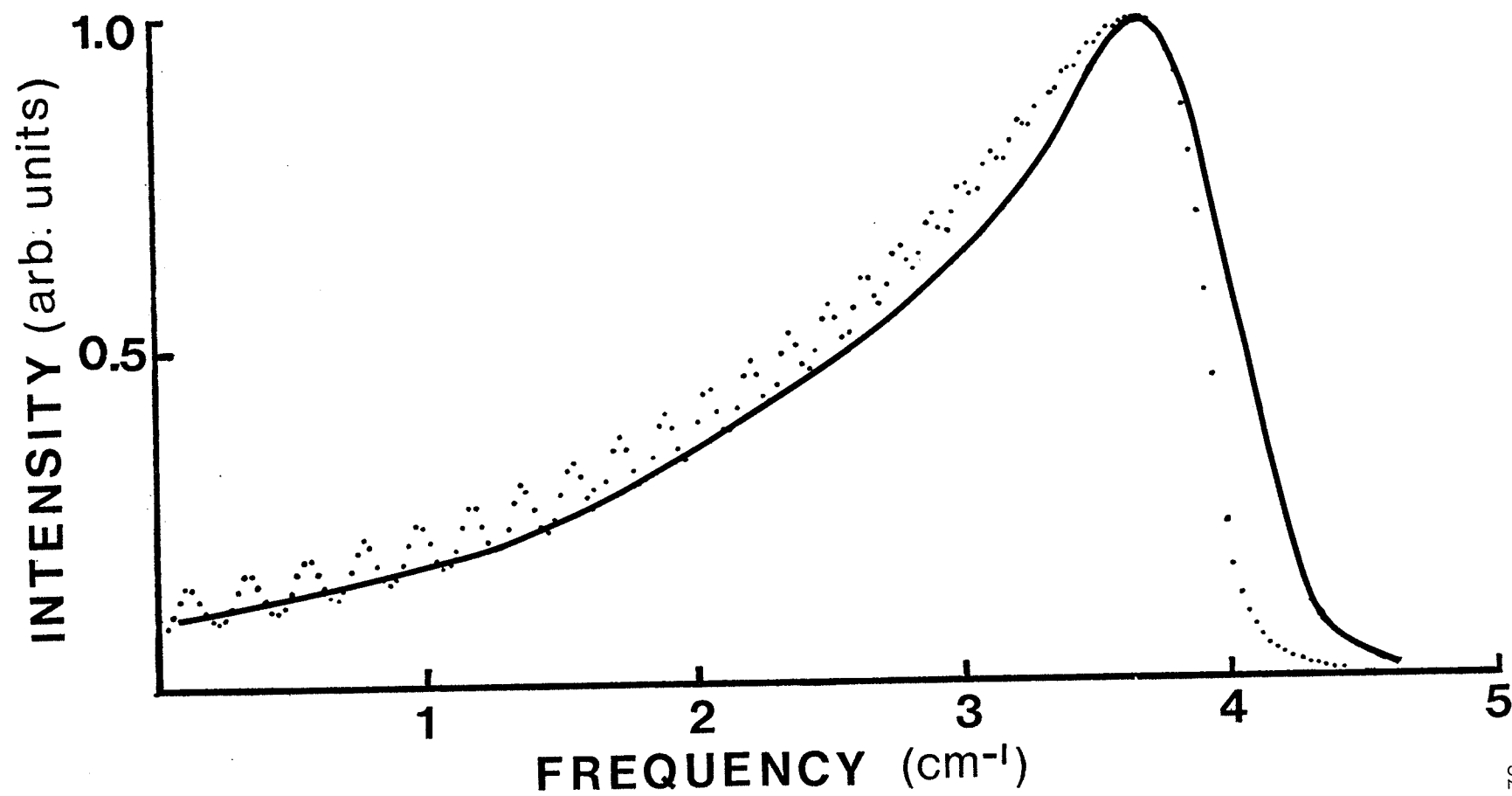
- (a) 2.2 amagat (pure N_2O)
- (b) 3.4 amagat
- (c) 7.7 amagat
- (d) 11 amagat
- (e) 17.3 amagat
- (f) 36.7 amagat
- (g) 71.2 amagat
- (n) 73.1 amagat
- (i) 129.6 amagat

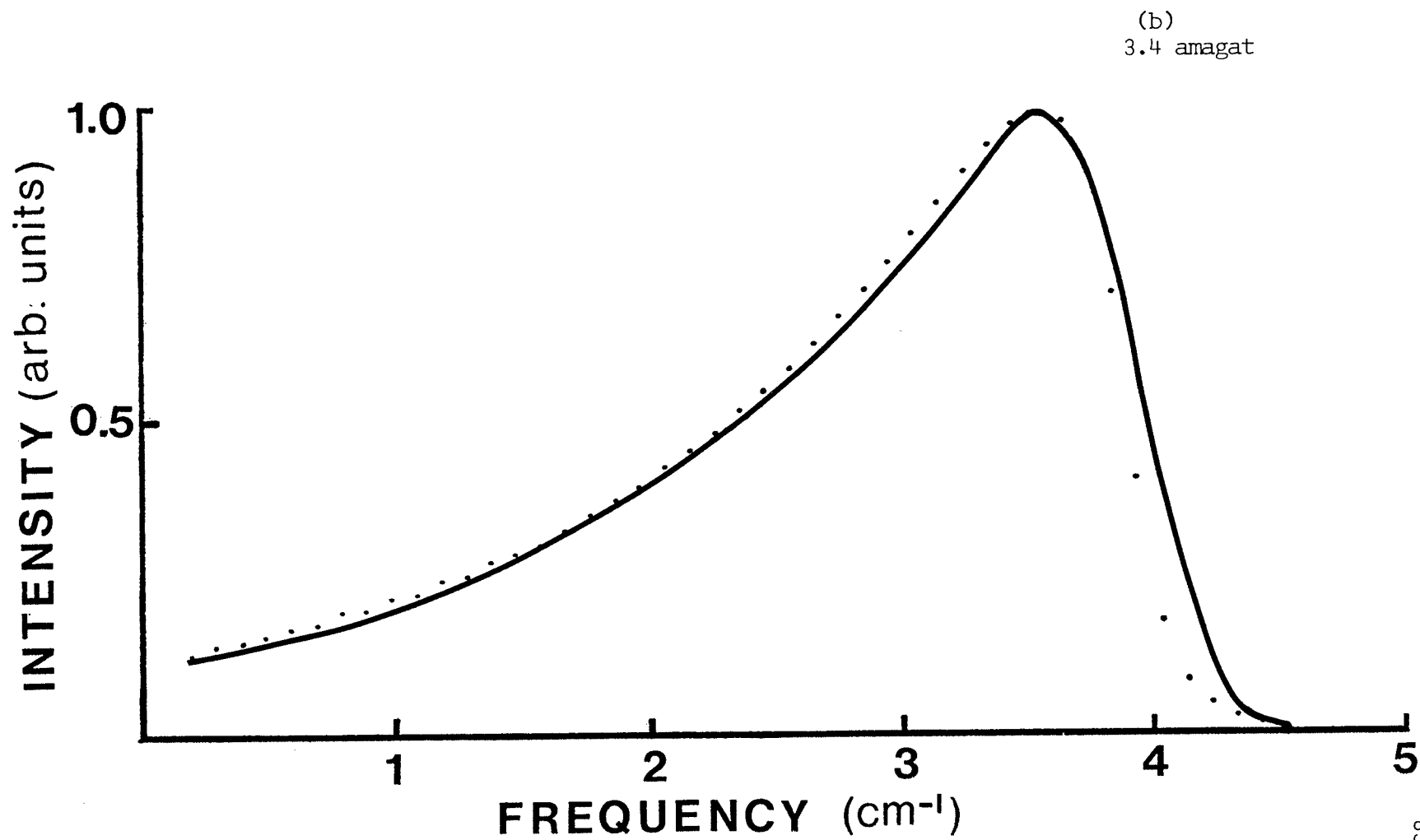
dots: theoretical lineshape

solid line: deconvoluted experimental lineshape

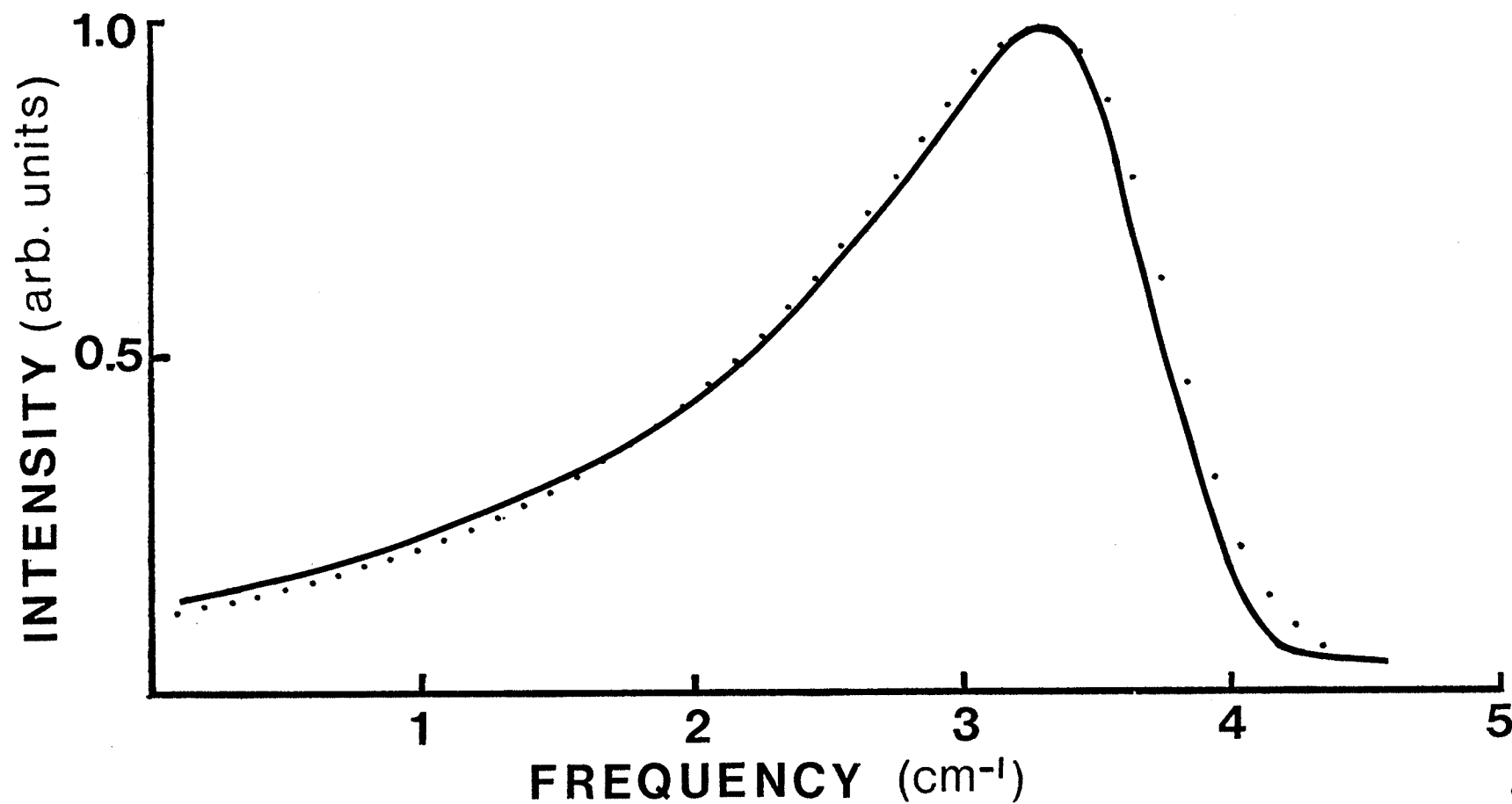
Frequency origin is arbitrary.

(a)
2.2 amagat

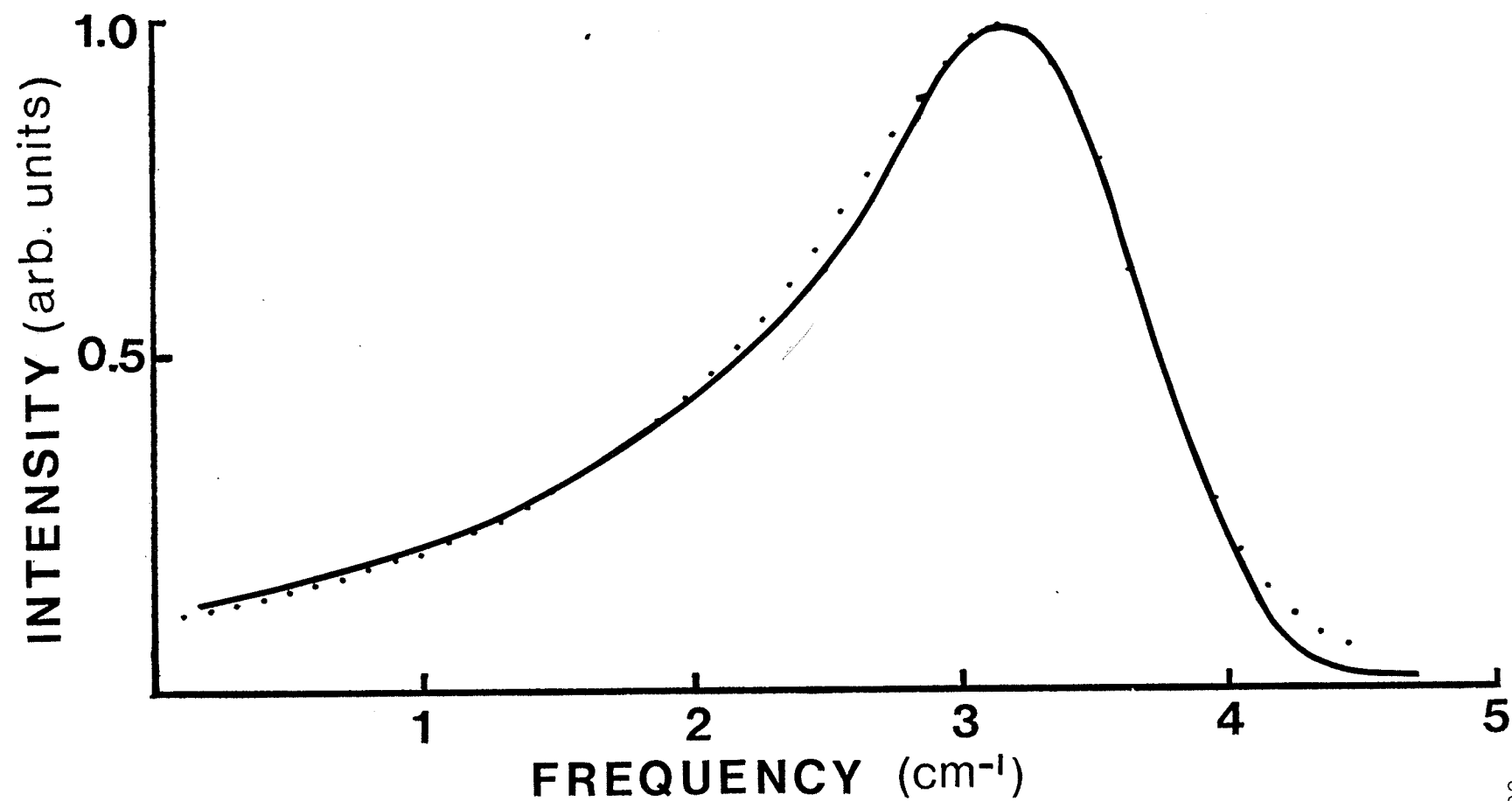




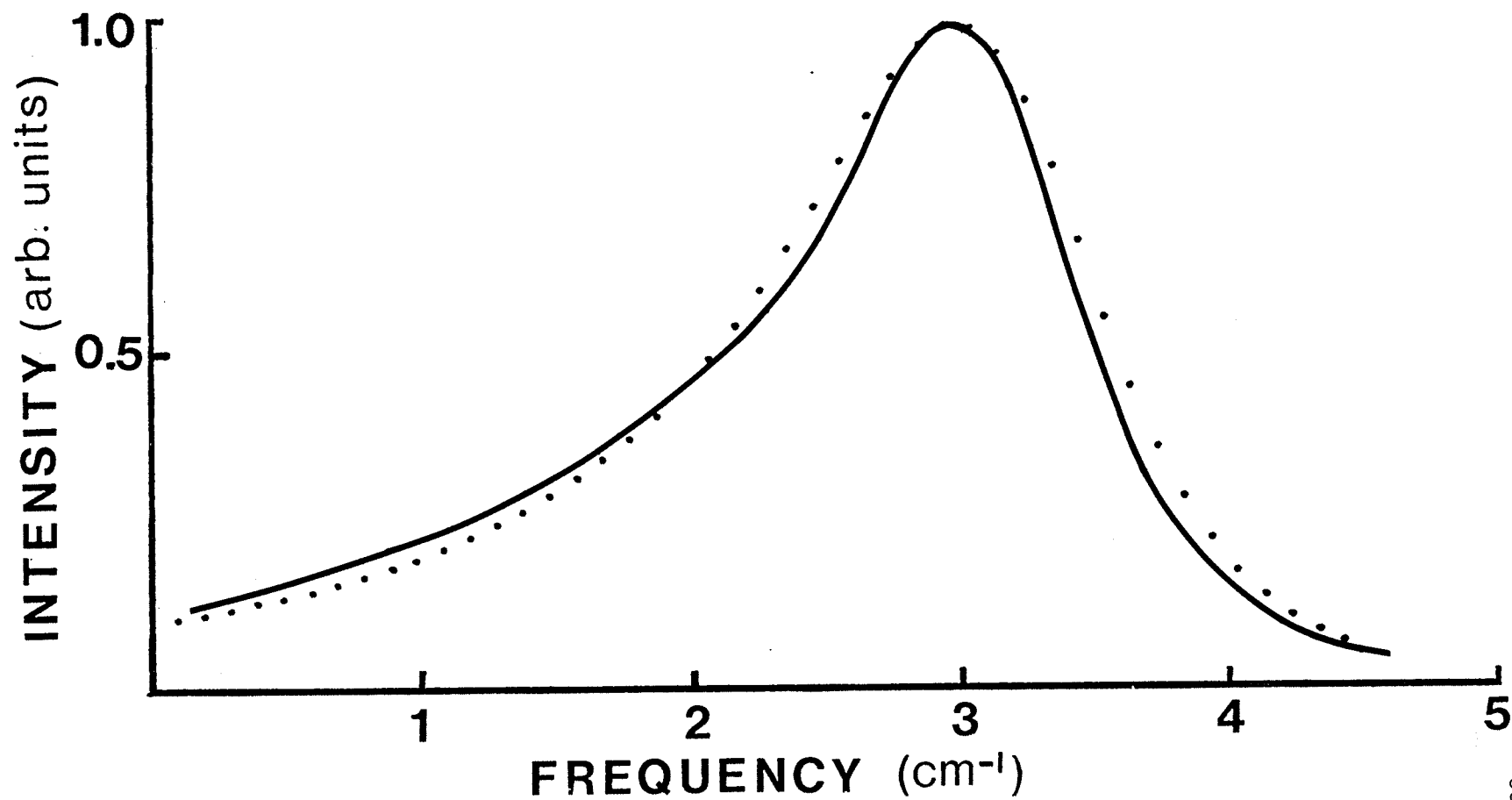
(c)
7.7 amagat



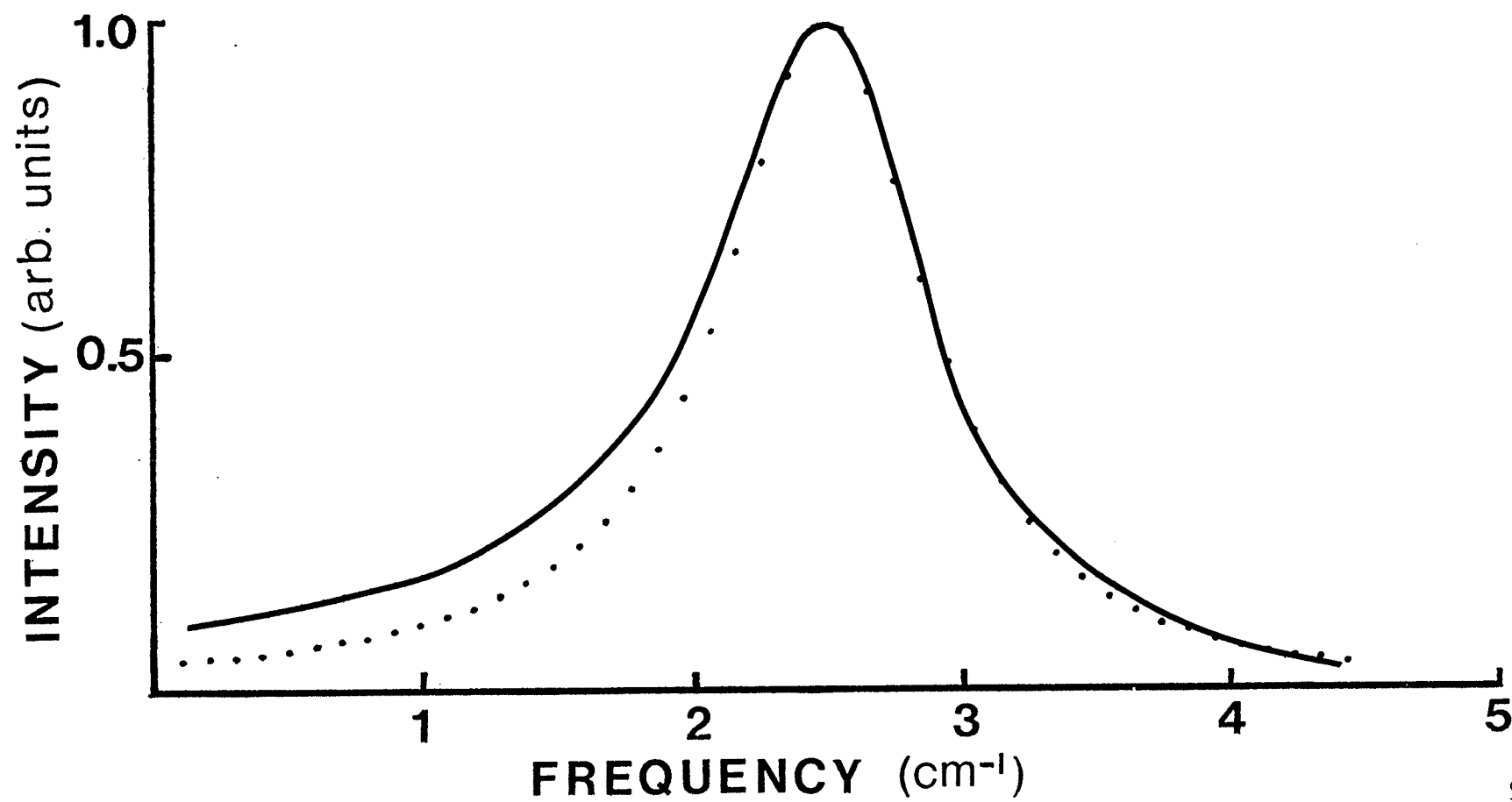
(d)
11 amagat



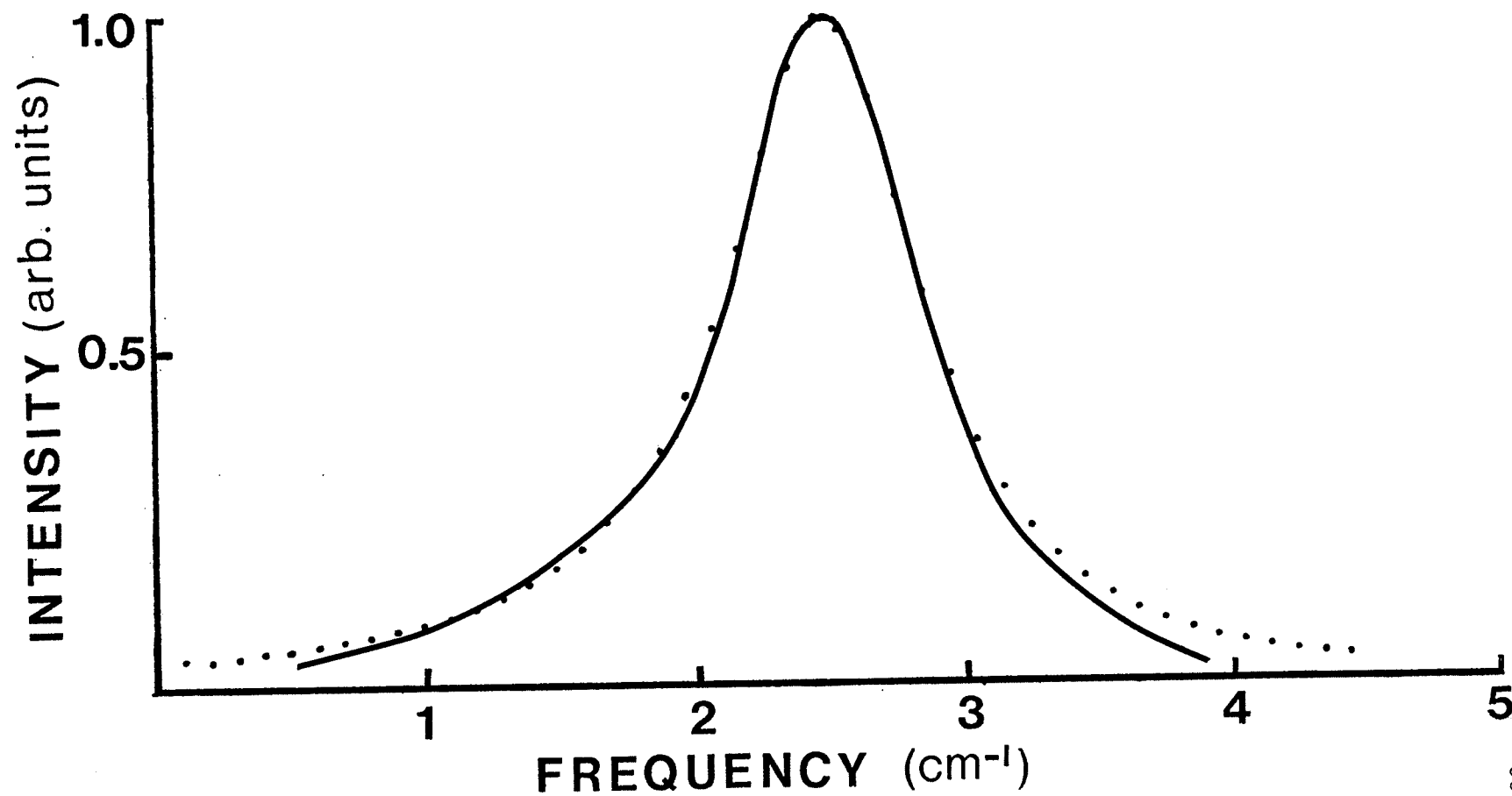
(e)
17.3 amagat



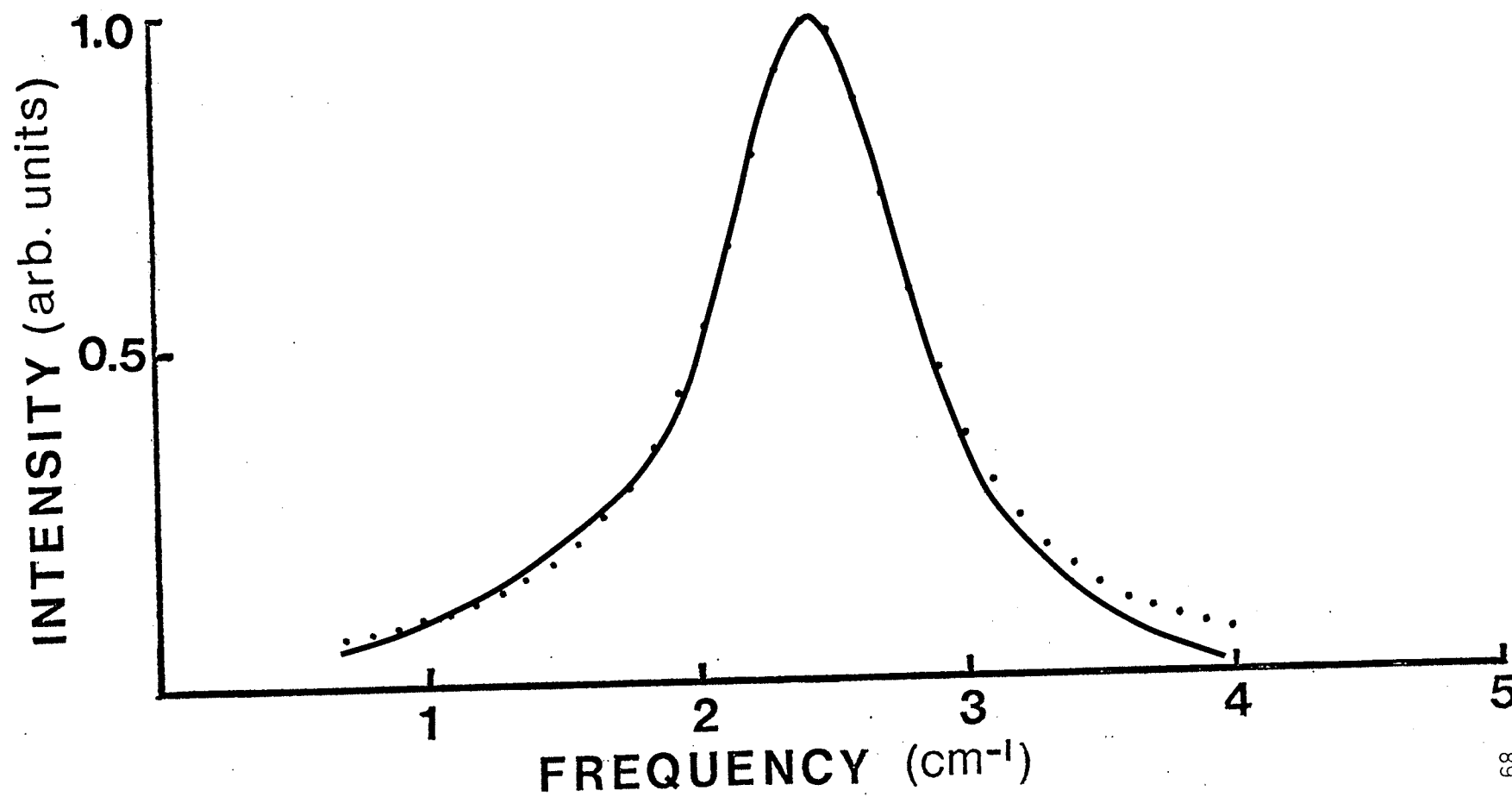
(f)
36.7 amagat



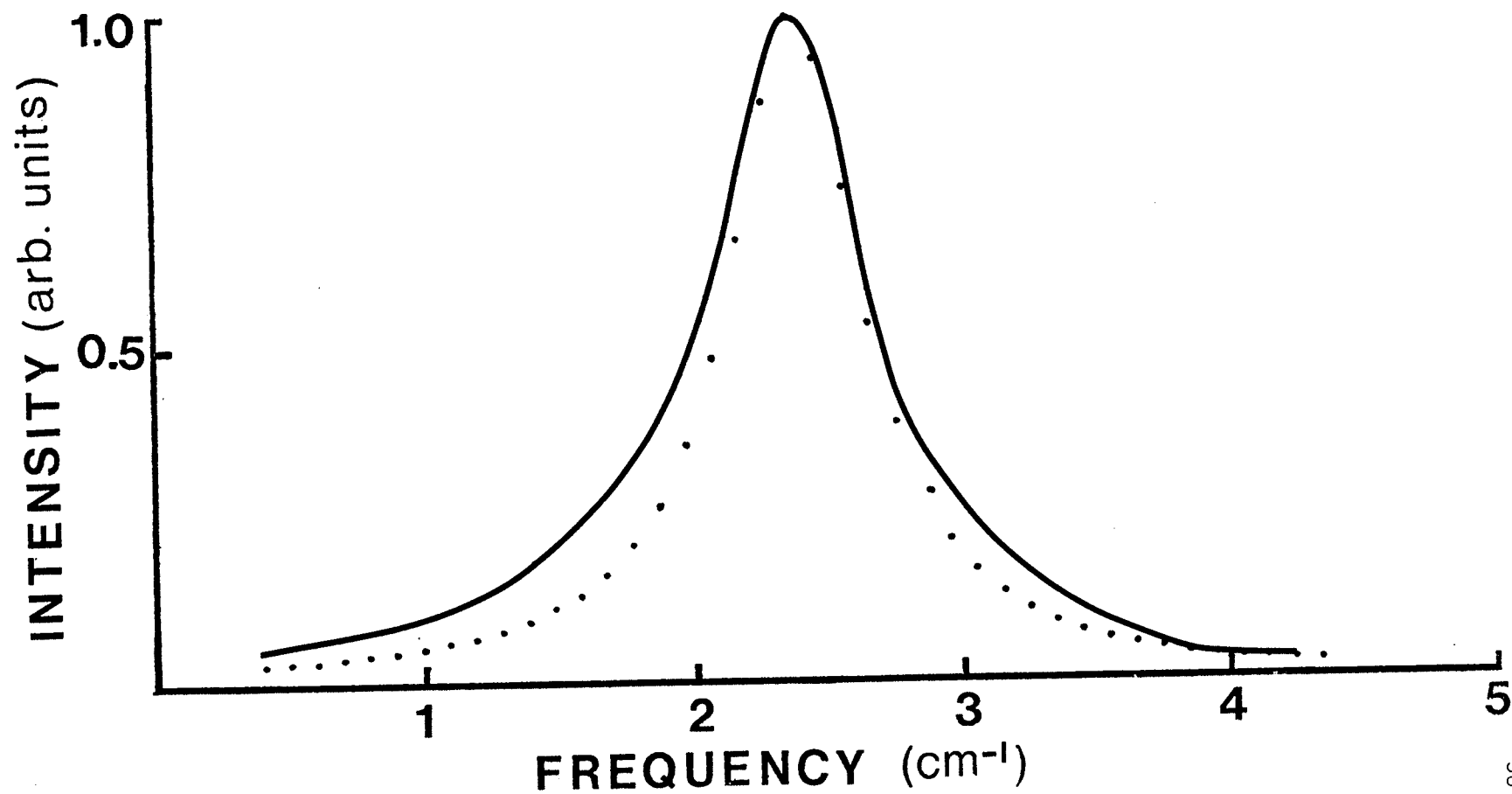
(g)
71.2 amagat



(h)
73.1 amagat



(i)
129.6 amagat



of the J-scrambling model and not only of the indirect-dephasing theory.

Above 73.1 amagat, our speculation is that perhaps direct dephasing is starting to be noticeable. It should also be noted however that at these high densities, the indirect-dephasing mechanism is still largely dominant.

5.2.4 Comparison between theory and experiment - ν_1 Q-branch

Though it proved convenient to calibrate the relaxation rate versus experimental density by using the linewidth results from ν_3 alone, self-consistency of the theory requires that the results obtained from ν_3 be transferable to ν_1 . The superimposed linewidth trends for ν_1 are exhibited in Fig. 5.3, in a manner similar to that for ν_3 . The motional narrowing of the ν_1 lineshapes is evident and agrees fairly well with the theoretical linewidth trend; this agreement is however not as good as for ν_3 .

We now consider the detailed lineshapes. As for the case of ν_3 , the theoretical ν_1 lineshapes are shown superimposed in Fig. 5.4 on their deconvoluted experimental counterparts so that their peaks coincide. In the calculation of the ν_1 theoretical lineshapes, we used the appropriate r -values obtained from the ν_3 -derived value of C_2 . The profiles have been normalised in the same manner as for ν_3 and, for the same reasons, the frequency origins are arbitrary. It is found that the ν_1 spectra exhibit progressive motional narrowing and symmetrisation with increasing perturbation. Table 4.1 and

FIG. 5.3

COMPARISON OF THEORETICAL AND EXPERIMENTAL
LINEWIDTH TRENDS - ν_1

solid line: logarithm of theoretical linewidth as function of
of relaxation rate b .

dots: logarithm of average experimental linewidth data,
plotted against logarithm of argon density n_2 .

The two horizontal scales are displaced so as to produce the best
agreement between the two trend lines.

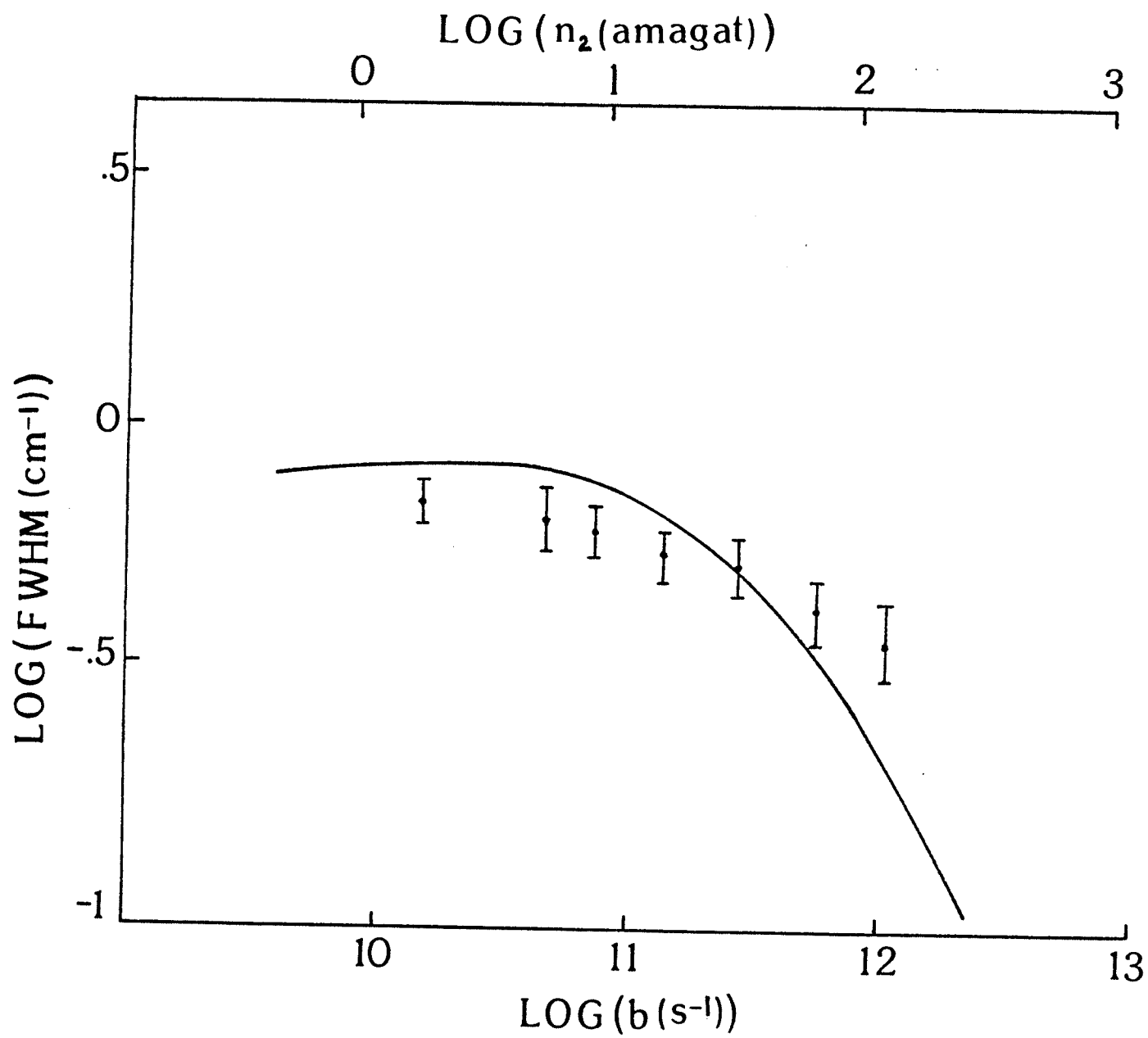


FIG. 5.4

COMPARISON OF THEORETICAL AND EXPERIMENTAL
LINESHAPES - ν_1

Except for (a), the specified density is that of the N_2O -Ar mixture.

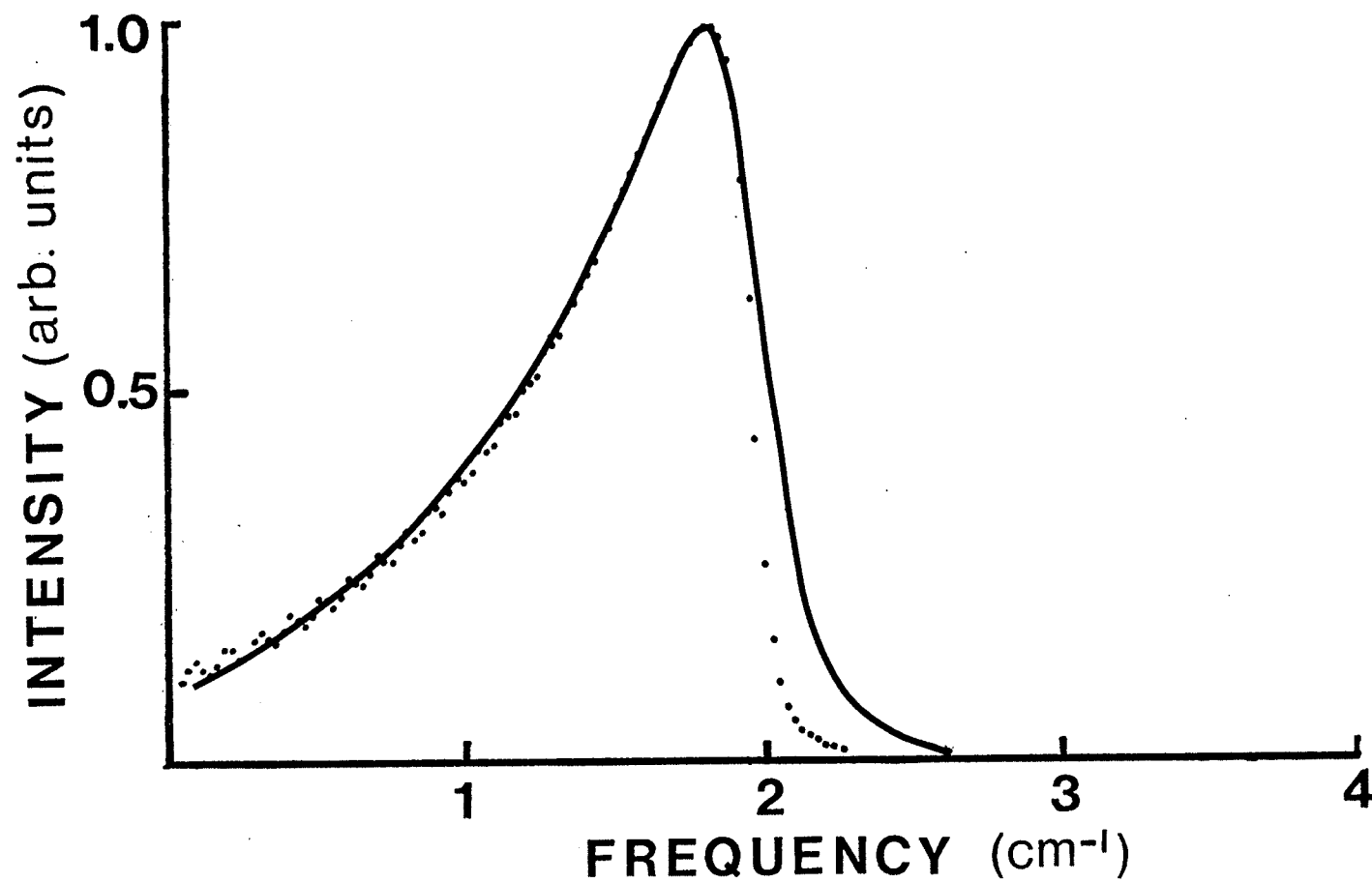
- (a) 1.6 amagat (pure N_2O)
- (b) 3.5 amagat
- (c) 7.3 amagat
- (d) 10.7 amagat
- (e) 18.6 amagat
- (f) 35.7 amagat
- (g) 73.6 amagat
- (h) 133.9 amagat

dots: theoretical lineshape

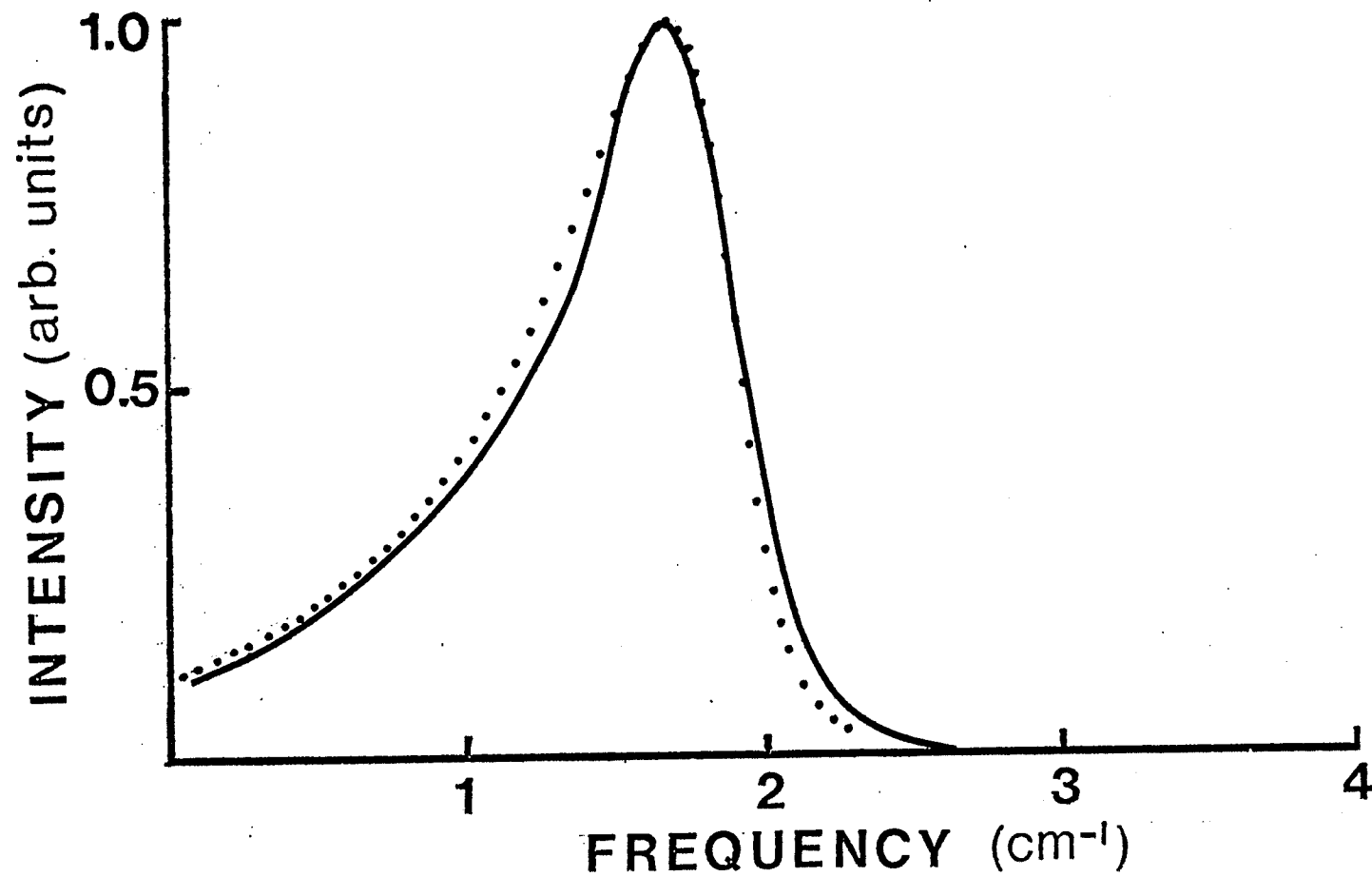
solid line: deconvoluted experimental lineshape

Frequency origin is arbitrary.

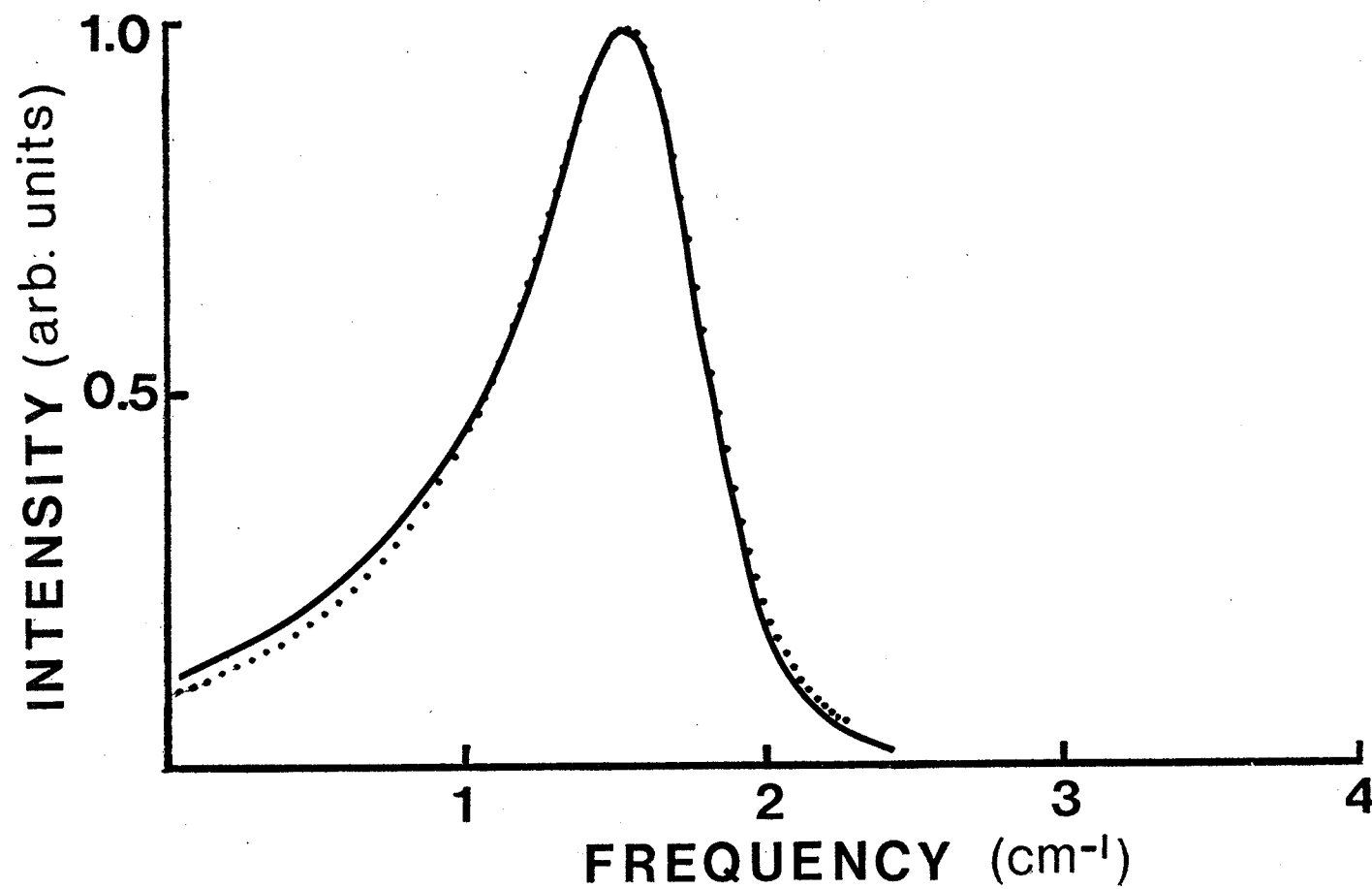
(a)
1.6 amagat



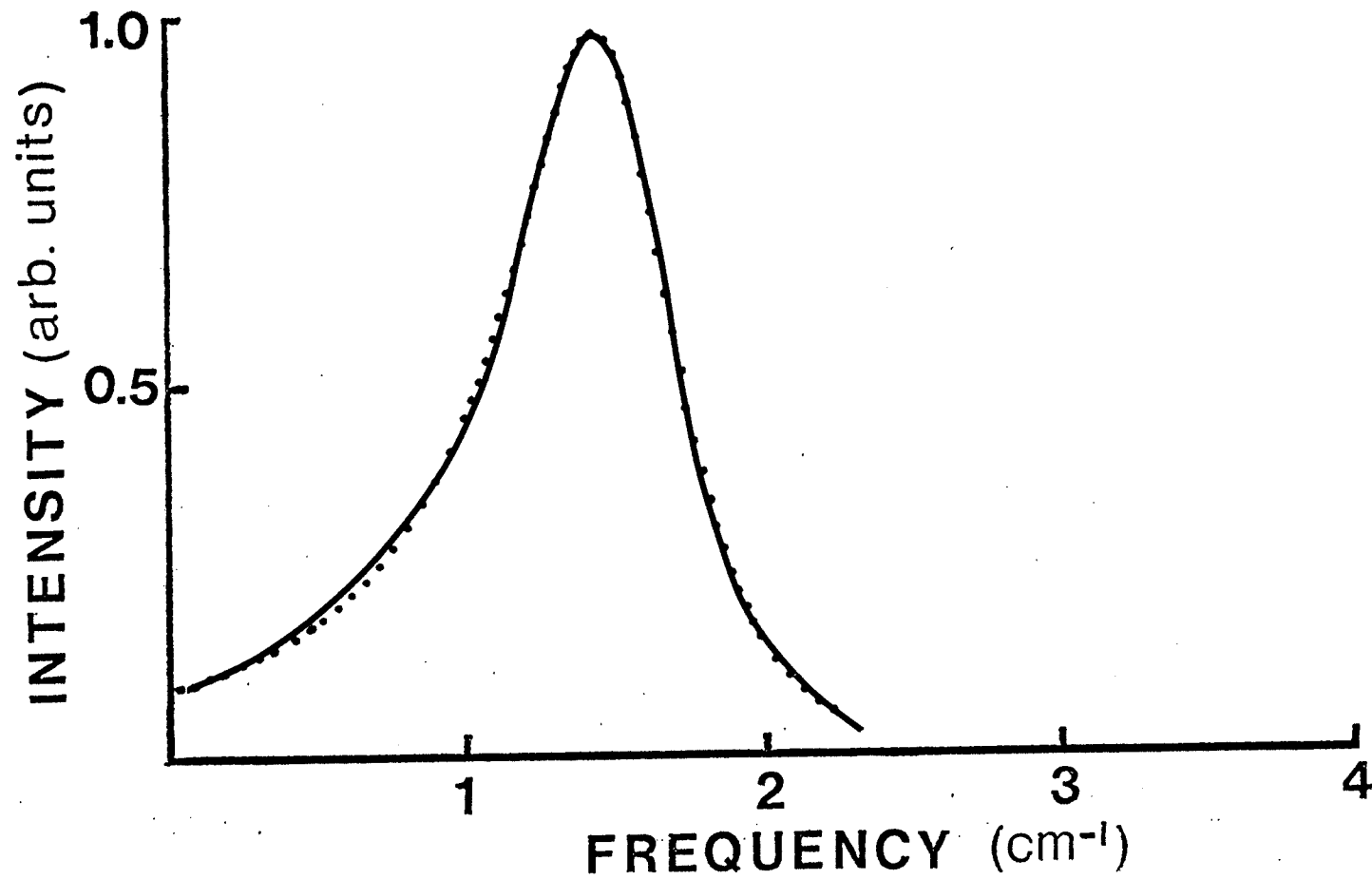
(b)
3.5 amagat



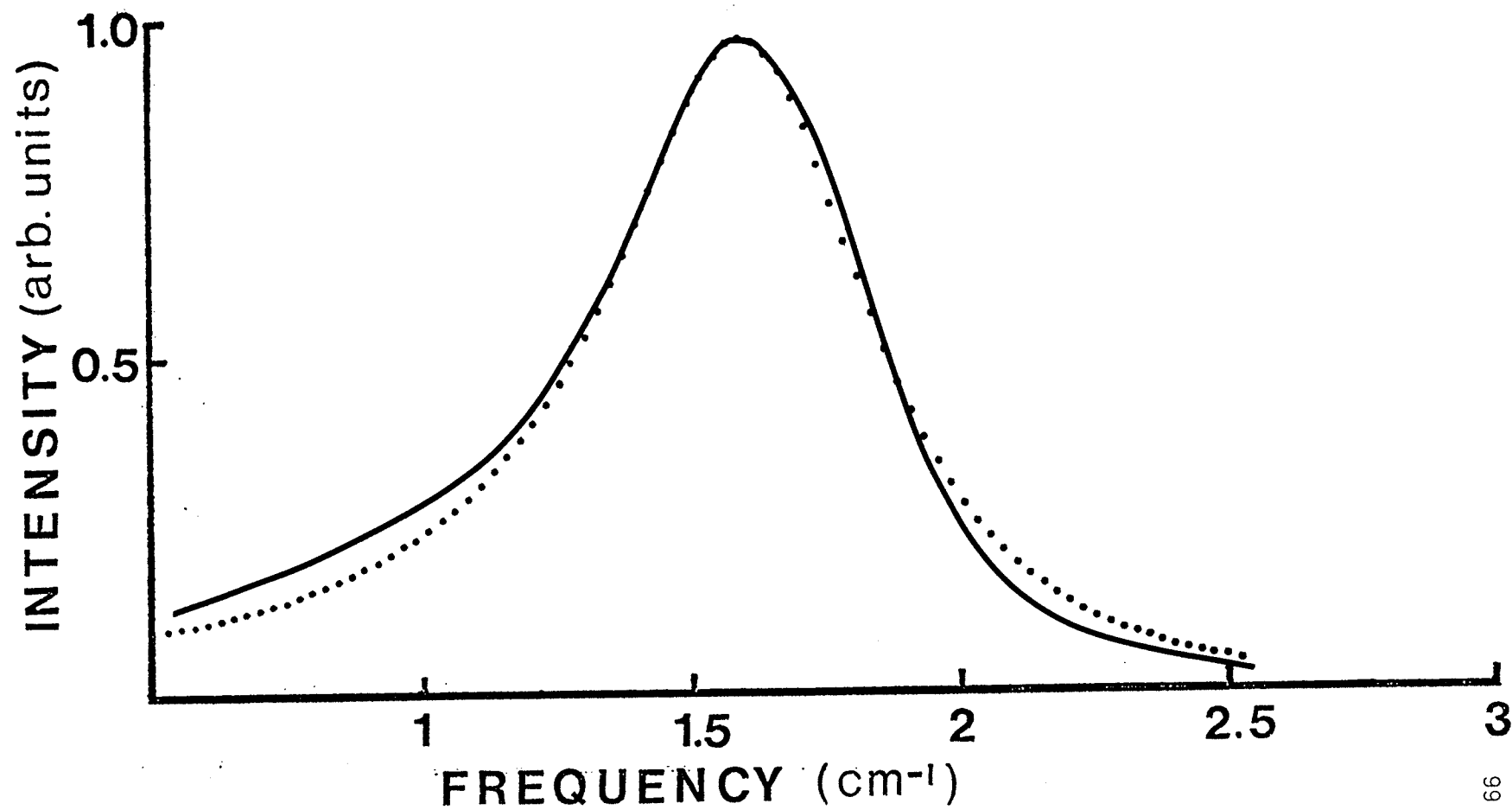
(c)
7.3 amagat



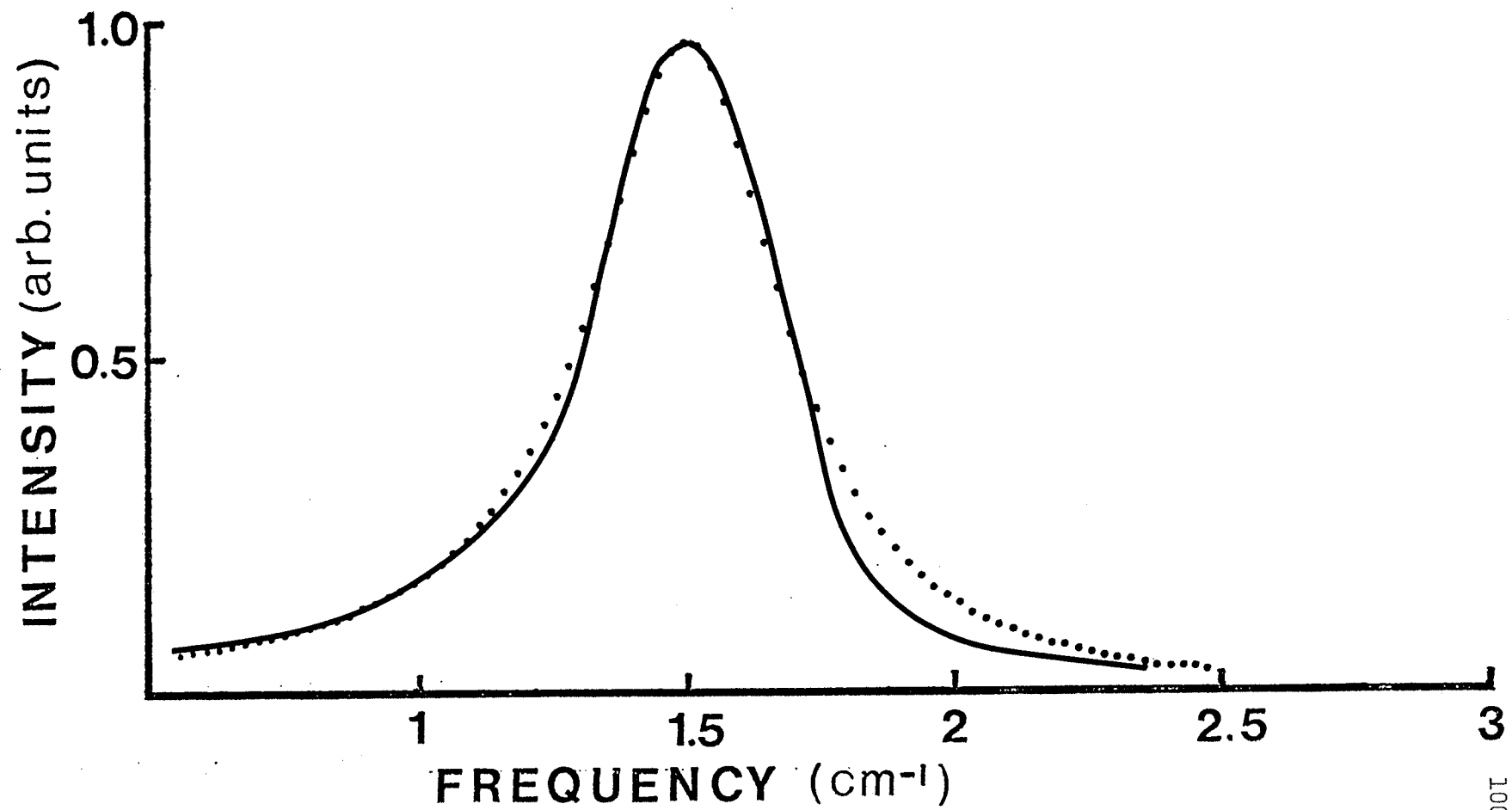
(d)
10.7 amagat



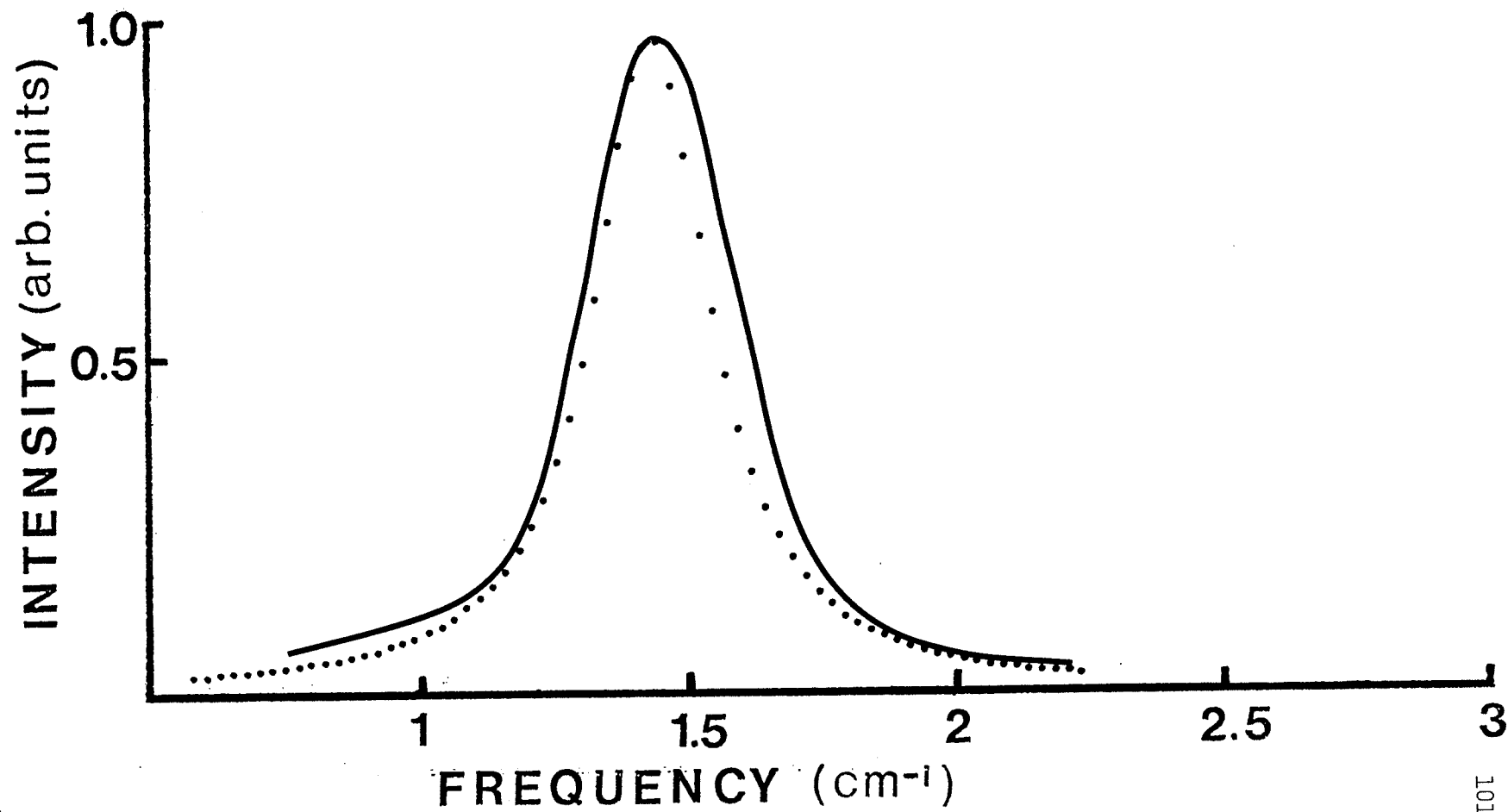
(e)
18.6 amagat



(f)
35.7 amagat



(g)
73.6 amagat



(h)
133.9 amagat

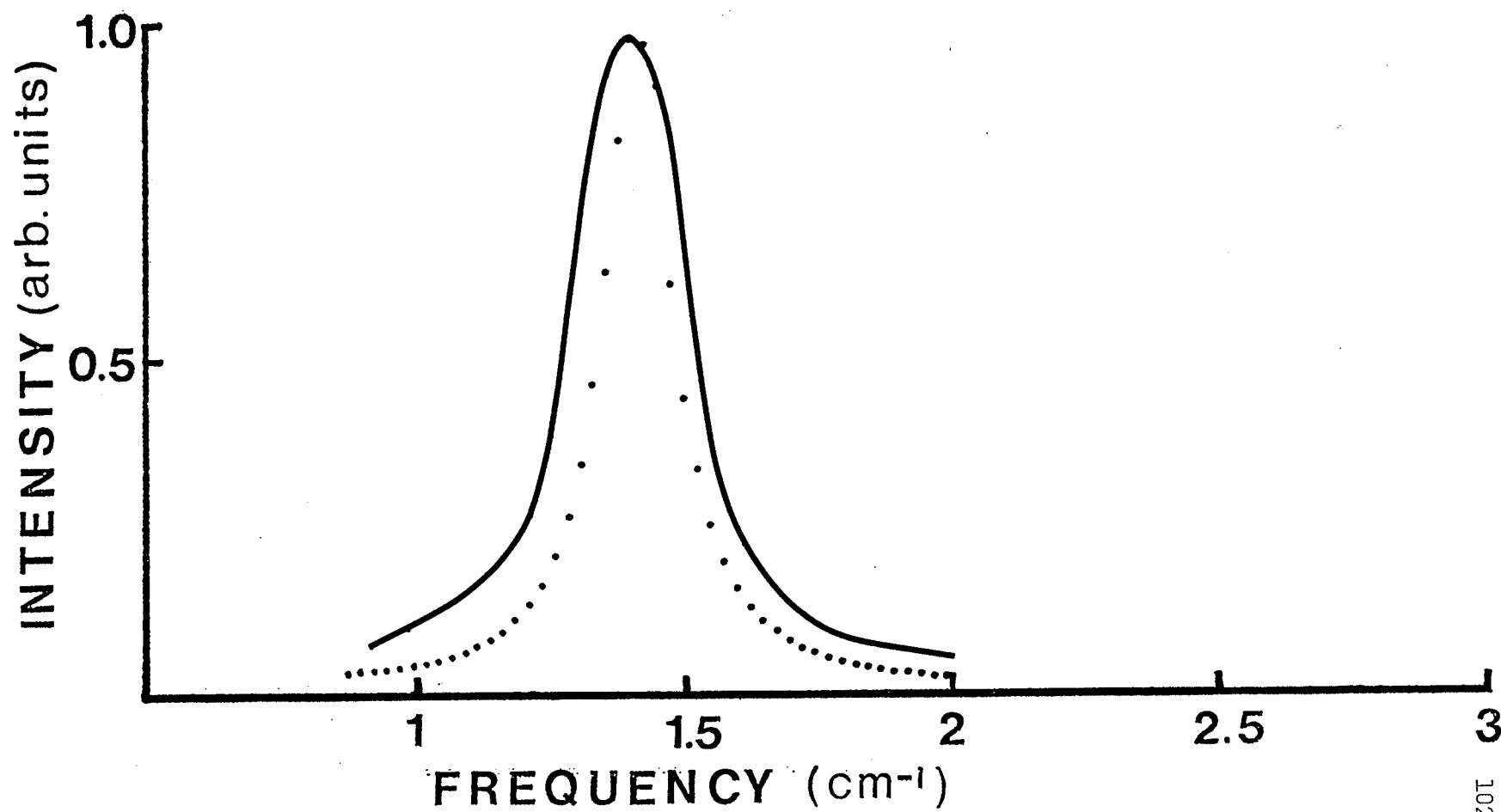


Fig. 5.4 both show convincing agreement between theoretical and experimental results up to 73.6 amagat. Here again, as for the ν_3 Q-branch, we speculate that the direct-dephasing mechanism might be starting to be prominent above 73.6 amagat. However, it should also be remarked that at the highest experimental density, the linewidth approaches the resolution limit of the spectrometer. Thus, the deconvolution method might not be able to reproduce the true lineshape even if the latter is physically narrower. This could be another reason for the discrepancy between the experimental and theoretical lineshapes at the highest density.

The theoretical spectrum at 1.6 amagat displays an apparent scatter which is due to the discrete rotational structure which survives at low relaxation rates. The spacings between rotational maxima are non-uniform and near the peak are smaller than the sampling interval. The irregular appearance occurs because consecutive sample points are as likely to fall both on rotational maxima as alternately on maxima and minima. The rotational structure is also apparent in the theoretical ν_3 spectrum at 2.2 amagat (see Fig. 5.2). However, it is so fine in comparison to the slit function that deconvolution does not reproduce it in the experimental spectrum of either vibrational mode, although it is present physically.

On the whole, the narrowing with increasing perturbation as well as the observed symmetrisation of the initially skewed profiles of both the ν_1 and ν_3 Q-branches serves to confirm the indirect-

dephasing theory. The results obtained are consistent with the findings of Kubo³ who first showed that any Markovian modulation scheme implies the eventual collapse of the lineshape into a symmetric Lorentzian as the modulation speeds up. Also, the fact that the value of $b:n_2$ is so successfully transferred to the ν_1 lineshapes supports the indirect-dephasing theory which asserts that the spectra are governed by a rotational relaxation scheme independent of either vibrational mode. Furthermore, justification of the use of the J-scrambling model is obtained from the agreement between predicted and experimental lineshapes.

5.3 Frequency Shift of Q-branch Lineshapes

As has been stated already, the indirect-dephasing theory predicts the gradual shift in peak frequency of the Q-branch lineshapes with increasing relaxation rate with the end result that the peak frequency coincides with the thermal average frequency ω_0 . In order to test this aspect of the theory, the gradual frequency shifts of the experimental lineshapes are compared to their theoretical counterparts. For this purpose, the experimental and theoretical peak shifts of Tables 4.4 and 4.6 are displayed in Figs. 5.5 and 5.6 for the ν_1 and ν_3 Q-branches respectively. It is found from Fig. 5.5 that good agreement between the experimental and theoretical peak shifts for the ν_1 Q-branch is obtained at all but the two highest densities of argon atoms. On the other hand, for the ν_3 Q-branch

FIG. 5.5

COMPARISON OF THEORETICAL AND EXPERIMENTAL
FREQUENCY SHIFT TRENDS - ν_1

solid line: theoretical peak frequency shift trend plotted
against logarithm of density n_2 of argon atoms.

dots: average experimental peak frequency shift data,
plotted against logarithm of density n_2 of argon
atoms.

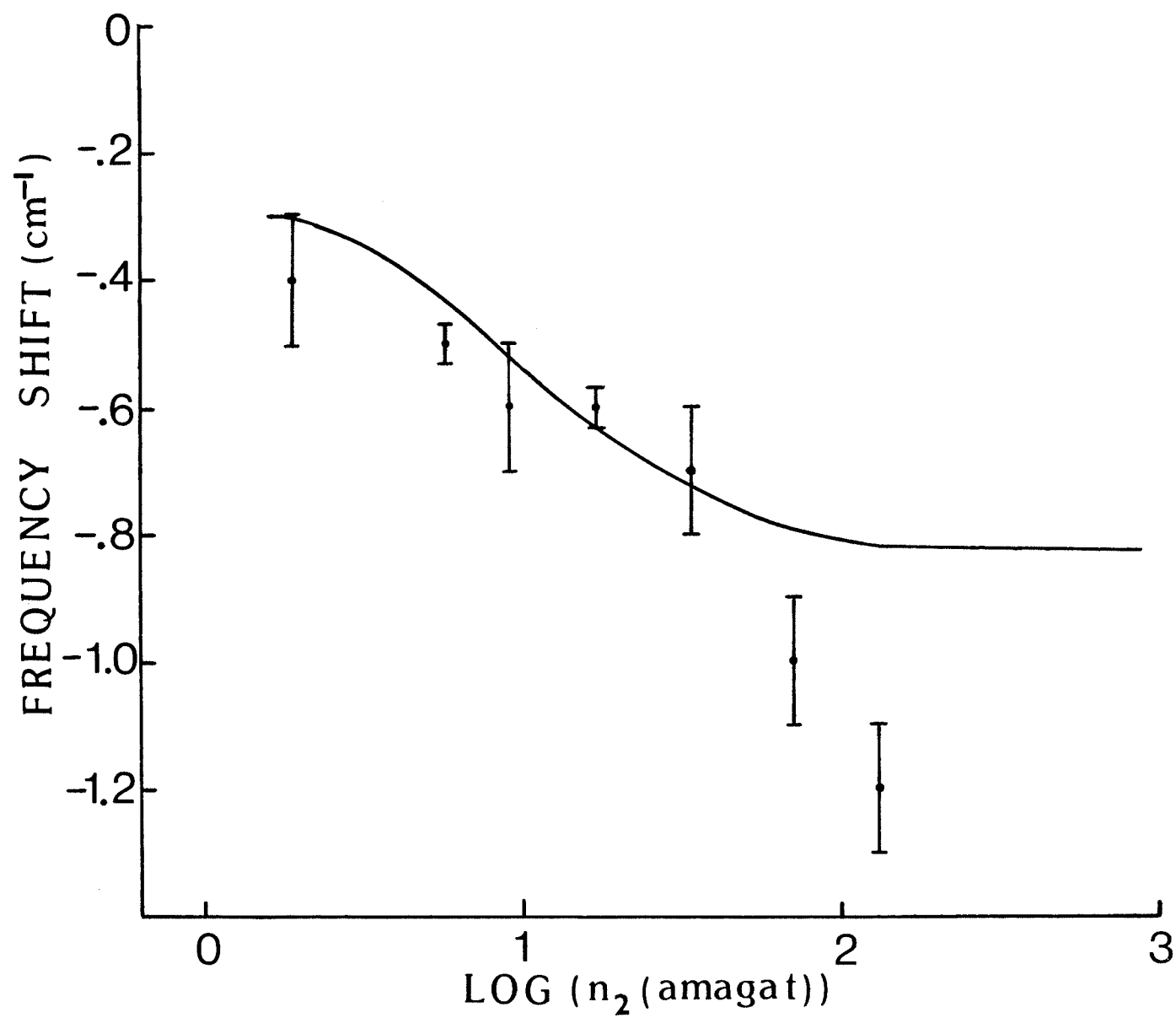


FIG. 5.6

COMPARISON OF THEORETICAL AND EXPERIMENTAL
FREQUENCY SHIFT TRENDS - ν_3

solid line: theoretical peak frequency shift trend plotted
against logarithm of density n_2 of argon atoms.

dots: average experimental peak frequency shift data,
plotted against logarithm of density n_2 of argon
atoms.

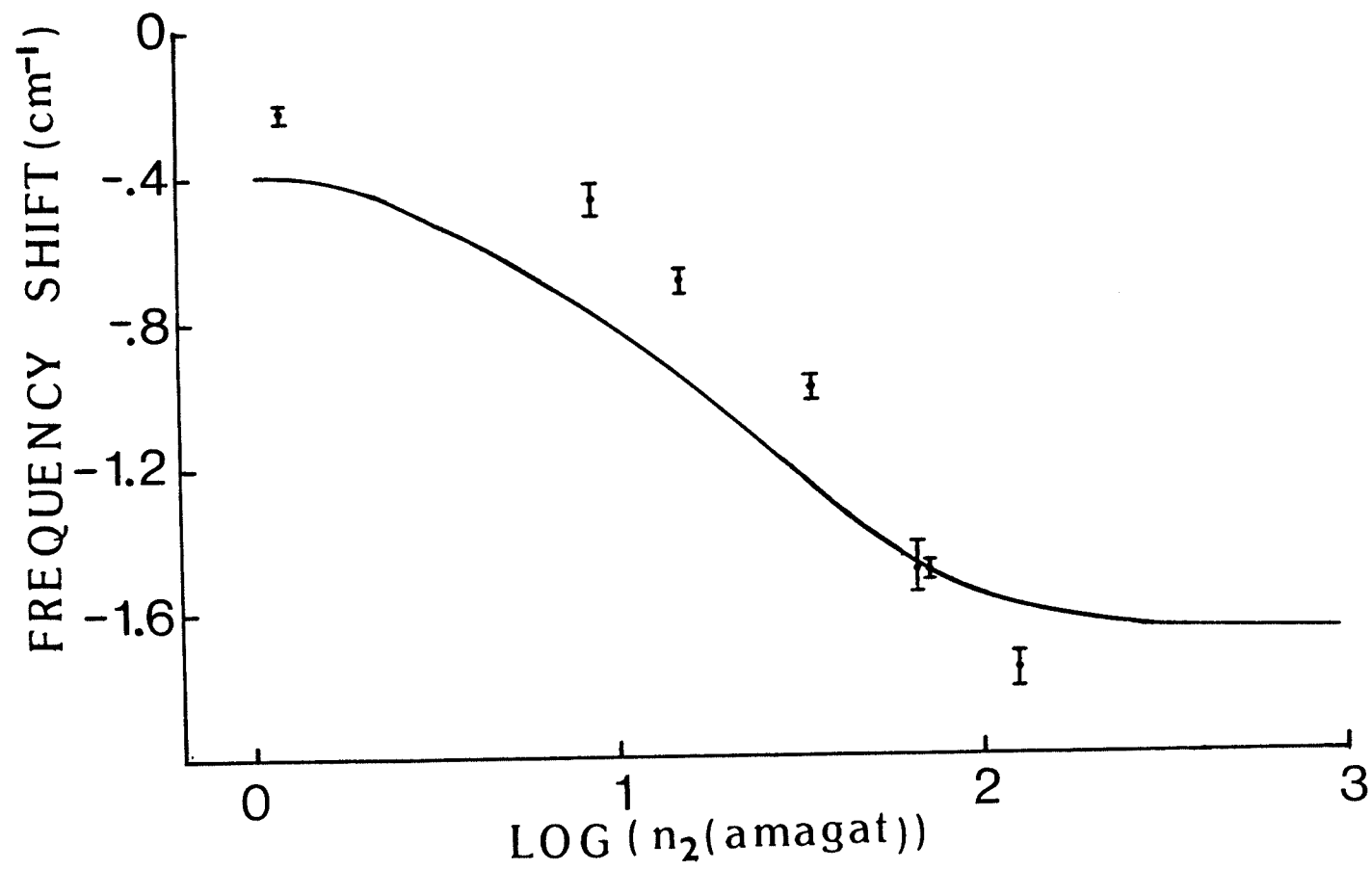


Fig. 5.6 shows that the experimental frequency shift trend is systematically less than the theoretical trend for the first four experimental densities. At the higher densities, the experimental peak frequency shifts agree fairly well with the predicted frequency shift trend. This is encouraging since it is an indication that in the regime of high relaxation rate the experimental ν_3 spectrum tends to collapse about its central frequency ω_0 , that is, its peak frequency coincides with ω_0 as predicted. However, from Fig. 5.5 it is seen that for ν_1 , this is not quite the case at the two highest experimental densities. The disagreement may perhaps be accounted for by either the incipient direct-dephasing process or the instrumental resolution problem alluded to earlier in §5.2.4. Just how the postulate that the peak frequency of the Q-branch lineshape coincides with the central frequency ω_0 at high relaxation rates is reconciled with the frequency shift interpretation here is now in order. When the peak frequency of the Q-branch lineshape becomes equal to ω_0 , then there will be a constant frequency difference between ω_0 and the reference frequency $Q(0)$. This is essentially the maximum peak frequency shift and is clearly depicted in Figs. 5.5 and 5.6 by the flattening of the theoretical peak frequency shift trend at high densities.

From the foregoing consideration of the peak frequency shifts of the ν_1 and ν_3 Q-branches, we may assert that the experimental results support the indirect-dephasing theory.

5.4 Effective Scrambling Diameter

The J-scrambling model described in §2.3 stipulates that each collision totally scrambles the rotational state. An effective diameter σ_R within which all collisions cause scrambling may be calculated on the basis of kinetic theory. We begin with the expression for the mean free path $\bar{\ell}_1$ for molecules of type 1 in a gaseous mixture of two different types of molecules (i.e. type 1 and type 2)³¹:

$$\bar{\ell}_1 = [4\sqrt{2}\pi n_1 r_1^2 + \pi n_2 (r_1 + r_2)^2 (\bar{v}_1^2 + \bar{v}_2^2)^{1/2} / \bar{v}_1]^{-1} \quad (5.7)$$

For our particular case of N₂O-Argon mixtures, we identify N₂O molecules and Ar atoms as being of type 1 and type 2 respectively. In

(5.7) we may then identify the following:

- n_1 = number density of N₂O molecules,
- n_2 = number density of Ar atoms,
- r_1 = radius of N₂O molecule,
- r_2 = radius of Ar atom,
- $\bar{v}_1$ = mean thermal velocity of N₂O molecules,
- and $\bar{v}_2$ = mean thermal velocity of Ar atoms.

The overall collision rate β_1 undergone by N₂O molecules is given by

$$\beta_1 = \frac{\bar{v}_1}{\bar{\ell}_1} = \bar{v}_1 [4\sqrt{2}\pi n_1 r_1^2 + \pi n_2 (r_1 + r_2)^2 (\bar{v}_1^2 + \bar{v}_2^2)^{1/2} / \bar{v}_1] \quad (5.8)$$

Here, we are primarily interested in β_{12} , that is, the component of β_1 due to collisions with Ar atoms. β_1 has another component β_{11} which is due to N_2O-N_2O collisions. β_{12} is just the value β_1 would have if $n_1 \rightarrow 0$.

From (5.8), we can write in the limit $n_1 \rightarrow 0$,

$$\beta_{12} = \pi n_2 (r_1 + r_2)^2 (\bar{v}_1^2 + \bar{v}_2^2)^{\frac{1}{2}}, \quad (5.9)$$

whence,

$$r_1 + r_2 = \{\beta_{12} / \pi n_2 (\bar{v}_1^2 + \bar{v}_2^2)^{\frac{1}{2}}\}^{\frac{1}{2}} \quad (5.10)$$

Since it is assumed that each collision induces rotational scrambling, then the ratio β_{12} / n_2 in (5.10) is equal to the ratio b/n_2 of §5.2.2, that is

$$\beta_{12} / n_2 = b / n_2 = C_2$$

where C_2 is as defined previously. The scrambling diameter σ_R may then be written as

$$\sigma_R = r_1 + r_2 = \{C_2 / \pi (\bar{v}_1^2 + \bar{v}_2^2)^{\frac{1}{2}}\}^{\frac{1}{2}} \quad (5.11)$$

Using the value of

$$C_2 = b : n_2 = 4.1 \times 10^{-16} \text{ s}^{-1} \text{ m}^3$$

obtained from our v_3 linewidth data and calculating the mean thermal velocities at 294 K to be

$$\bar{v}_1 = 375 \text{ ms}^{-1}$$

$$\bar{v}_2 = 393 \text{ ms}^{-1}$$

it is found that

$$\sigma_R = 4.9 \text{ \AA}$$

The effective scrambling diameter σ_R is close to the hard-sphere diameter σ for N_2O -Ar collisions which is given by

$$\sigma = (\sigma_1 + \sigma_2)/2 = 4.0 \text{ \AA}.$$

σ_1 is the hard-sphere diameter for N_2O - N_2O collisions and its value is $4.6 \text{ \AA}$ (from second virial coefficients).³² $\sigma_2 = 3.4 \text{ \AA}$ (from second virial coefficients)³² is the hard-sphere diameter for Ar-Ar collisions.

The effective scrambling diameter in the N_2O -Ar mixtures is slightly larger than in the pure N_2O gas where it was calculated to be $3.9 \text{ \AA}$.

In view of the kinetic-theory analogy on which (5.11) is based to hold, σ_R should be a critical impact parameter within which a collision will cause total J-scrambling and outside which J will be unaffected.

It is encouraging that σ_R turns out to be close to σ from the standpoint of the J-scrambling model. This result indicates that the

scrambling rate is about the same as the kinetic-theory collision rate, just as one expects if every collision thermalises the rotational state. Despite the success of the model, one should not ignore the various approximations that have been made here. In the first instance, the N_2O molecule is linear and therefore the hard-sphere concept used to obtain σ_R is incorrect. Consequently, the formula derived earlier for σ_R is inexact and therefore not too much reliance must be placed on exact agreement between the values of σ_R and σ . One could presumably correct for the relation between $\beta_{12}:n_2$ and molecular dimensions to allow for a non-spherical shape without changing the J-scrambling model. Secondly, the postulate that all collisions cause rotational scrambling is also inaccurate. In view of the diversity of molecular velocities, it cannot be expected that all collisions at any given impact parameter be sufficiently energetic to completely thermalise the rotational state, as is assumed by the model. The model is thus inherently approximate. Any serious shortcoming in the model would significantly affect the lineshapes in a many-level system. But in view of the success achieved earlier in predicting the lineshapes, it is remarkable that the J-scrambling model seems to be a good working basis.

5.5 Comparison of Present Findings with Previous Work

The present findings about the narrowing of the Raman Q-branches of N_2O in gaseous mixtures with argon conform with the

expectations first mentioned in §1.4. It is found that the narrowing of both the ν_1 and ν_3 Q-branches persists at all pressures studied. This is in contrast to the observed case of motional narrowing in pure N_2O gas^{14,15}. In particular, in pure N_2O gas, the narrowing of the ν_1 Q-branch was found to become obscured at about 25 amagat and was subsequently overtaken by collision broadening attributable to direct dephasing. For the ν_3 Q-branch, no clear onset of narrowing of the lineshape was observed; instead, motional narrowing was revealed by a reduction in the broadening rate of the collision-broadened profile. In the present work, we find that the use of argon atoms as perturbers leads to the narrowing of both the ν_1 and ν_3 lineshapes at all densities studied. In particular, the effect of direct dephasing in both Raman Q-branches is clearly found to have been negligible up to a density of about 73 amagat.

The present work also confirms the narrowing of the Raman Q-branches of N_2O in gaseous mixtures with argon; this narrowing was first observed by Ouillon¹⁷ as stated in Chapter 1. Ouillon also reported the pressure-dependent peak frequency shifts with respect to the peak frequency at 1 atm of N_2O gas. However, no direct comparison of our frequency shift measurements can be made with Ouillon's since we have used different amount of N_2O and argon gas in the experiments. For example, we kept the N_2O concentration at 2 atm whereas Ouillon had 10 atm of N_2O ; also we have used different concentrations of Ar gas in the mixtures. A comparison could presumably have been made if

the frequency shifts reported by Ouillon had been reckoned relative to the peak frequency at zero density, that is, essentially the frequency of $Q(0)$ as we have done. Nevertheless, if our frequency shifts are taken relative to the peak frequency at the lowest pressure studied, an order of magnitude comparison with the frequency shift data of Ouillon reveals fairly good agreement over roughly similar range of densities.

For much the same reasons stated above, the linewidth data of Ouillon cannot be directly compared with our linewidth data. Also, in spite of having been corrected for instrumental distortion, the linewidth data reported by Ouillon were not obtained from the explicit deconvolution of the lineshapes as we have done in the present work. However, both Ouillon's and our linewidth data are of the same order of magnitude over roughly equivalent changes in density.

Just as in the previous work on pure N_2O gas^{14,15}, the broadening of the individual components $Q(J)$ of the vibrational Q -branches alluded to in Chapter 1 could not be resolved in our experiments at the lowest densities used.

CHAPTER 6

CONCLUSIONS

6.1 Indirect Vibrational Dephasing

Our findings serve to confirm that the vibrational relaxation of the Q-branches of the N_2O molecule proceeds via an indirect dephasing process. More specifically, molecular collisions without affecting the vibrational behaviour directly, nonetheless cause vibrational frequency changes indirectly by inducing transitions between rotational states with which the vibration is coupled. The molecule oscillates at a new resonance frequency for a finite time interval at the end of which phase coherence with the original oscillation is destroyed, that is, dephasing occurs. Also, the assumption that the vibrational dephasing process is Markovian in nature holds strongly. It is observed that the measured N_2O Q-branch lineshapes are consistent with the indirect dephasing mechanism at nearly all densities studied.

6.2 J-Scrambling Model

We find that the particular scheme of rotational relaxation based on the J-scrambling model together with the indirect-dephasing theory correctly predicts the evolution of the Q-branch lineshapes with increasing density. Given the large number of populated rotational levels at room temperature, the success of the J-scrambling model is particularly significant.

6.3 Direct Dephasing

As expected, we observe that by using argon atoms as perturbors of the vibrational Q-branches, the narrowing of the lineshapes persists up to considerably high densities. In particular, it is found that the direct-dephasing mechanism is clearly insignificant in both the ν_1 and ν_3 vibrational Q-branches up to a density of about 73 amagat.

6.4 Frequency Shift of the Q-branch Lineshapes

The experimental peak frequency shifts, within limits of the experiments, are found to be consistent with those predicted by the indirect-dephasing theory, thus providing additional support for the theory just mentioned.

6.5 Effective Diameter for Rotational Scrambling

The effective scrambling diameter σ_R is found to be close to the hard-sphere diameter. It is encouraging that σ_R turns out to be close to what is anticipated from kinetic theory. In this regard, the J-scrambling model used for defining the scheme of rotational relaxation in order to predict the N_2O lineshapes turns out to be a good working basis. This is confirmed by the match obtained between theoretical and empirical linewidth trends.

APPENDIX

Centroid Problem

The location of the centroid of a given Q-branch spectrum was calculated from the formula

$$\bar{\omega} = \frac{\sum I_i \omega_i}{\sum I_i}$$

where I_i = intensity in the i^{th} channel, that is, essentially the number of counts in that channel,

and ω_i = frequency of the i^{th} channel which is assigned an arbitrary value. ω_i increases by 0.1 cm^{-1} in going from one channel to the next.

The main objective here is to show that the magnitude Δ described in §4.4.2 is invariant under deconvolution. To that end, we conversely prove that the centroid of any distribution $f(x)$ is shifted by the same amount upon convolution with a particular function $S(x)$ (which is identified as the slit function), independently of the choice of $f(x)$.

We assume, without loss of generality, that both $f(x)$ and $S(x)$ are area-normalised:

$$\text{i.e.} \quad \int_{-\infty}^{\infty} f(x) dx = 1 \quad (1)$$

$$\int_{-\infty}^{\infty} S(x) dx = 1 \quad (2)$$

Let $\bar{x}$ denote the centroid of $f(x)$. Then

$$\bar{x} = \int_{-\infty}^{\infty} dx \, x \, f(x) \quad (3)$$

Now, let $\bar{x}_S$ denote the centroid of the function resulting from the convolution $S(x) * f(x)$. Since $S(x) * f(x) = \int_{-\infty}^{\infty} dx' \, S(x-x')f(x')$, we have

$$\begin{aligned} \bar{x}_S &= \int_{-\infty}^{\infty} dx \, x \int_{-\infty}^{\infty} dx' \, S(x-x')f(x') \\ \text{or } \bar{x}_S &= \int_{-\infty}^{\infty} dx' \, f(x') \int_{-\infty}^{\infty} dx \, x \, S(x-x') \end{aligned} \quad (4)$$

The inner integral may be evaluated by using the substitution $u = x-x'$ as shown in the following:

$$\begin{aligned} \int_{-\infty}^{\infty} dx \, x \, S(x-x') &= \int_{-\infty}^{\infty} du \, (u+x') \, S(u) \\ &= x' \int_{-\infty}^{\infty} S(u) du + \int_{-\infty}^{\infty} S(u) u \, du \end{aligned} \quad (5)$$

Upon substitution of (2) in (5), we obtain

$$\int_{-\infty}^{\infty} dx \, x \, S(x-x') = x' + c \quad (6)$$

where $c = \int_{-\infty}^{\infty} S(u) u \, du$ is actually the centroid of the slit function. We note that c is independent of $f(x)$.

Now, upon insertion of (6) in (4), we obtain

$$\begin{aligned}\bar{x}_S &= \int_{-\infty}^{\infty} dx' f(x') (x' + c) \\ &= \int_{-\infty}^{\infty} dx' f(x') x' + c \int_{-\infty}^{\infty} f(x') dx' \\ &= \bar{x} + c\end{aligned}$$

Thus, on convolving $f(x)$ with $S(x)$, the centroid of $f(x)$ is shifted by c , independently of the choice of function $f(x)$. With the use of this result and reference to Fig. 4.4, we find that if we deconvolute Fig. 4.4(c), the centroids of both the ν_3 and Ne spectra get shifted by the same amount with the result that the separation Δ between them is unchanged.

In the following, further description of the method of calculating the centroid is in order. It was found that to locate the position of the true centroid with an error less than 0.1 cm^{-1} , it was necessary to include in the calculation the region of the line-shape which extends at least 8 cm^{-1} to the left of the peak. The region beyond this boundary (shown as the shaded area in Fig. 1) can be neglected.

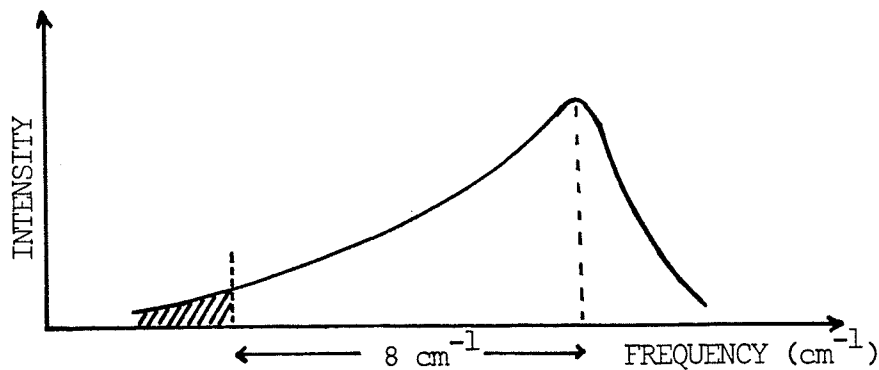


Fig. 1

However, in most cases the recorded spectra actually did not extend quite far enough in the left wing so that it was impossible to implement the condition just mentioned. Alternatively, we chose to locate the centroid of the lineshape by truncating the tail situated beyond 3 cm^{-1} to the left of the peak as shown in Fig. 2.

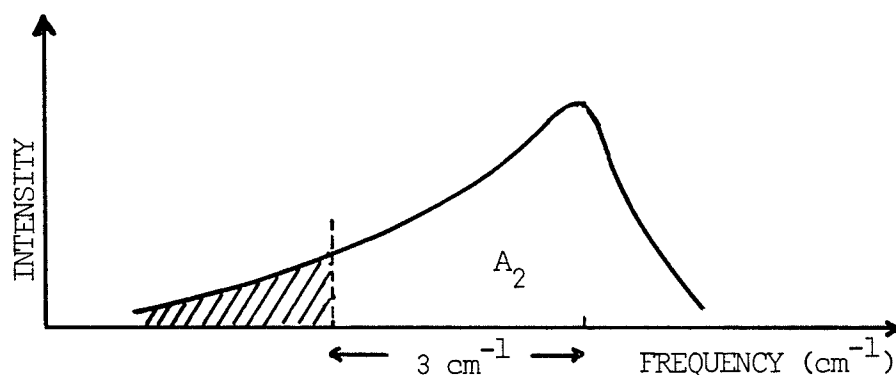


Fig. 2

This method in fact does not permit us to locate the true centroid of the overall lineshape; all it gives is the centroid of the region A_2 which is indeed only an approximation to the true centroid of the overall deconvoluted lineshape. However, the merit of this method is that it enables us to find the location of a point on the spectrum, namely the centroid of region A_2 , to which an absolute frequency may be assigned. This precisely serves for the purpose of frequency calibration which is of primary interest. We shall call the centroid of the non-neglected region A_2 of the lineshape the "pseudo-

centroid" of the overall lineshape.

In order to show that the technique of §4.4.2 applies equally well to pseudo-centroids, we shall now prove that the pseudo-centroid undergoes the same shift in position as does the true centroid when convolution (or deconvolution) is performed. This statement holds only when the part of the lineshape ignored in the pseudo-centroid calculation is slowly varying with respect to frequency, that is, the tail is almost linear in every small frequency interval. For example, in Fig. 2, the shaded area may be ignored because the function is nearly linear in that region.

It will be useful to look at what convolution does to a function that is nearly linear. Suppose we have a function $f(x) = ax + b$ where a and b are constants, then,

$$\begin{aligned} S(x) * f(x) &= \int_{-\infty}^{\infty} dx' S(x-x') (ax'+b) \\ &= a \int_{-\infty}^{\infty} dx' S(x-x') x' + b \int_{-\infty}^{\infty} dx' S(x-x') \\ &= a \int_{-\infty}^{\infty} dx' S(x-x') x' + b.1 \end{aligned}$$

with the use of the substitution $u = x-x'$, we have

$$\int_{-\infty}^{\infty} dx' S(x-x') x' = \int_{-\infty}^{\infty} du S(u) (u-x)$$

$$= - \int_{-\infty}^{\infty} du u S(u) + x \int_{-\infty}^{\infty} du S(u)$$

$$= -c + x ,$$

where c is defined as previously.

$$\therefore S(x) * f(x) = a(x-c) + b$$

Hence, $f(x)$ is translated by c along x -axis. That is, $S(x) * f(x)$ has same value at $x + c$ as f had at x .

Now, suppose we divide the lineshape into two regions of area A_1 and A_2 , A_1 being a region of almost linear variation. (See Fig. 3).

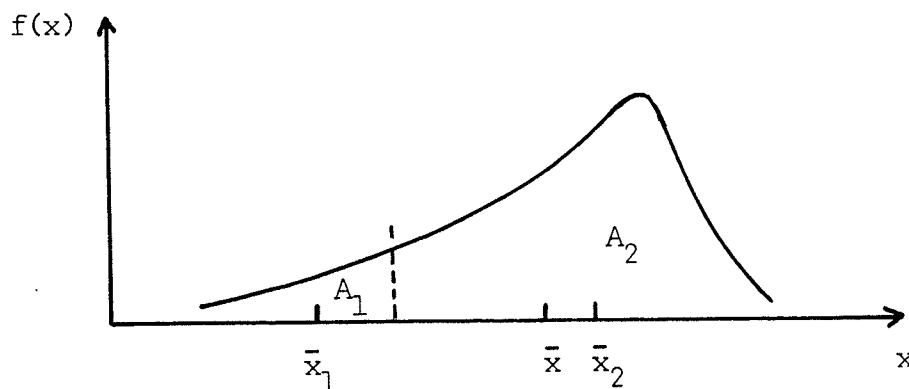


Fig. 3

In Fig. 3, $\bar{x}_1$ is the centroid of A_1 , $\bar{x}_2$ of A_2 and $\bar{x}$ of $A_1 + A_2$.

Consider the result of convolving this lineshape. Suppose we obtain the lineshape displayed in Fig. 4.

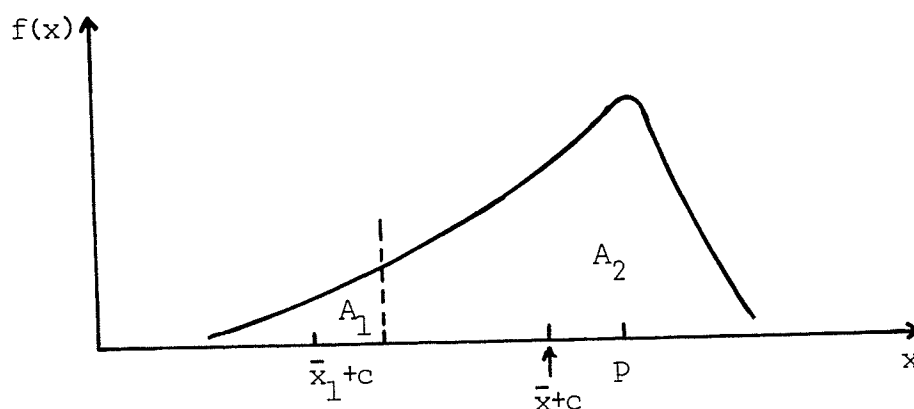


Fig. 4

By previous arguments, the centroid of the overall convolved lineshape is located at $\bar{x} + c$. From the foregoing result for linear functions, the centroid of A_1 is located at $\bar{x}_1 + c$. It should be noted that the boundary between A_1 and A_2 on the convolved lineshape is at the same point on the tail of lineshape as before convolution. It is possible to speak of "same point" because convolution does not distort tail of lineshape; as we have seen, it merely translates the tail.

With the area normalisation conditions (1) and (2), the convolved lineshape therefore has same total area as before. Also, area A_1 is clearly the same as before convolution. Therefore, area A_2 must likewise be the same as before (though lineshape is otherwise distorted in this region). With the further normalisation convention: $A_1 + A_2 = 1$, the centroid of overall lineshape may be

expressed as the weighted average:

$$\bar{x} = A_1 \bar{x}_1 + A_2 \bar{x}_2 \quad (7)$$

Similarly, for the centroid after convolution:

$$\bar{x} + c = A_1 (\bar{x}_1 + c) + A_2 p \quad (8)$$

where p (pseudo-centroid of overall lineshape) is the unknown centroid of A_2 .

Upon subtraction of (7) from (8) we have

$$c = A_1 c + A_2 (p - \bar{x}_2)$$

$$\text{or } p - \bar{x}_2 = c (1 - A_1)/A_2$$

Since $A_2 = 1 - A_1$,

$$\Rightarrow p = \bar{x}_2 + c$$

Thus, the pseudo-centroid $\bar{x}_2$ is also shifted by c to $\bar{x}_2 + c$ after convolution just like $\bar{x}_1$ and $\bar{x}$.

Now, we have to establish contact between the way the pseudo-centroid was defined above (with reference to a boundary drawn at

a particular point on tail of lineshape) and the operational definition we have actually used to calculate pseudo-centroids (i.e. the centroid of a region extending a fixed distance to one side of itself). It is important to check if this convention really defines the same boundary between A_1 and A_2 before and after convolution. It is helpful to look at the problem in reverse. If boundaries were indeed the same before and after convolution, then calculated pseudo-centroids should be the same distance from the boundary before and after convolution. We recall that all centroids and the boundary itself were simply displaced by c under deconvolution, given our original definition of the boundary. Thus if we set ourselves the problem of picking out the same boundary after convolution as we had selected before convolution, this boundary must satisfy the condition we have set in practice: it must be the same distance from the pseudo-centroid as it was before convolution. If this condition determines the boundary uniquely, we must thereby have found the correct location for the boundary.

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