

SPECTROSCOPY OF JET-COOLED AROMATIC AMINES

by

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ABSTRACT

An investigation was made of the electronic spectroscopy of selected jet-cooled aromatic amines. The internal degrees of freedom of the gas phase molecules are cooled under collision-free conditions: molecular vibrations to less than 50K and molecular rotations to less than 5K. The prepared molecules were then investigated by laser induced fluorescence (LIF) from which wavelength resolved and time resolved studies were made.

Initial work was concerned with the molecule 4-N,N-dimethylaminobenzonitrile (DMABN), of interest, because of its unusual fluorescence properties in polar solutions. DMABN exhibits an anomalous a^* emission red-shifted from the normal b^* emission. No single, simple model accounts for the complicated excited state dynamics observed in the solution phase. The investigation of DMABN and like molecules was conducted under jet-cooled conditions in order to clarify results observed in the solution phase.

Excitation and dispersed fluorescence spectra and fluorescence lifetimes of DMABN and its van der Waals complex with methanol were recorded. An attempt was made to create and detect the red-shifted state in the jet but it was not observed. Although, 1:1 DMABN solvent

complexes were formed exhibiting hypsochromic spectral shifts relative to the bare molecule. The results were consistent with a non-emissive a^* state under jet-cooled conditions.

The LIF spectra of 4-aminobenzonitrile (4-ABN) and its complexes with small polar solvents were compared to the results for DMABN. 4-ABN resembles aniline in its spectroscopy, with the amino inversion mode being active in both excitation and dispersed fluorescence spectra.

Finally, the spectroscopy of 4-ABN and DMABN was compared to that of N-methylaniline, N,N-dimethylaniline and 2- and 3-aminobenzonitrile in terms of the large amplitude motions active in the amino group.

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CONTENTS

	PAGE NUMBER
ABSTRACT	2
ACKNOWLEDGEMENTS	4
CONTENTS	5
LIST OF FIGURES	9
LIST OF TABLES	14
CHAPTER 1: GENERAL INTRODUCTION	16
1.1 INTRODUCTION	17
1.2 SOLVENT EFFECTS ON PHOTOPHYSICAL PROCESSES	17
1.2.1 Specific solute-solvent interactions	20
1.3 THE ANOMALOUS FLUORESCENCE BEHAVIOUR OF DMABN	22
1.3.1 The observation of dual fluorescence	22
1.3.2 The TICT state hypothesis	27
1.3.3 Kinetics of the TICT State	33
1.3.4 The role of specific solute-solvent interactions	37
i) exciplex formation	37
ii) 3-electron sigma bonding	41
1.3.5 Other compounds with TICT states	42
1.3.6 Conclusion for DMABN	45
1.4 VAN DER WAALS MOLECULES	46
1.5 NON-RADIATIVE DECAY	49
1.5.1 Intramolecular vibrational redistribution	51
1.6 VIBRATIONAL MODES OF BENZENE	55
REFERENCES	58

CHAPTER 2:	EXPERIMENTAL	64
2.1	THE SUPERSONIC JET	65
2.1.1	Supersonic jet, theory of	65
2.1.2	Variation of temperature with distance from the nozzle	68
2.1.3	Sample density variation with distance from the nozzle	71
2.1.4	Residence time in excitation beam	71
2.1.5	Formation of van der Waals complexes	73
2.1.6	Vibrational and rotational temperature	74
2.1.7	Supersonic jet, experimental	75
2.2	THE MEASUREMENT OF FLUORESCENCE EXCITATION SPECTRA	80
2.2.1	Method	80
2.2.2	Excitation source	82
2.2.2a	The excimer laser	82
2.2.2b	The dye laser	92
2.2.2c	Second harmonic generation	98
2.2.3	The photomultiplier tube	103
2.2.4	The gated integrator and boxcar averager	104
2.3	THE MEASUREMENT OF DISPERSED FLUORESCENCE SPECTRA	106
2.4	THE MEASUREMENT OF FLUORESCENCE LIFE-TIMES	108
2.4.1	The excitation source	111
2.4.1a	The mode-locked ion laser	111
2.4.1b	The dye laser	112
2.4.2	Second harmonic generation	113
2.4.3	The micro-channel plate photomultiplier tube	114

2.5	EXPERIMENTAL DETAILS	116
CHAPTER 3:	SPECTROSCOPY OF 4-N,N-DIMETHYLAMINO-BENZONITRILE AND ITS VAN DER WAALS COMPLEXES: THE ABSENCE OF THE TICT STATE	122
3.1	INTRODUCTION	123
3.2	EXPERIMENTAL	125
3.3	RESULTS	127
3.3.1	Excitation spectrum of DMABN	127
3.3.2	Dispersed fluorescence spectra of DMABN	133
3.3.3	Fluorescence decay lifetimes	138
3.3.4	DMABN-methanol complexes	142
3.3.5	DMABN-higher alcohol complexes	143
3.4	DISCUSSION	146
3.4.1	The bare molecule	146
3.4.2	Non-radiative decay channels	147
3.4.3	DMABN-alcohol complexes	149
	REFERENCES	154
CHAPTER 4:	SPECTROSCOPY OF 4-AMINOBENZONITRILE AND ITS VAN DER WAALS COMPLEXES	156
4.1	INTRODUCTION	157
4.1.1	Absence of TICT emission in 4-ABN	157
4.1.2	Inversion vibration of the amino group	160
4.1.3	B-type double-headed rotational contours	166
4.2	EXPERIMENTAL	170
4.3	RESULTS AND DISCUSSION	171
4.3.1	The bare molecule	182
4.3.2	4-ABN complexes	182

i)	4-ABN-Ar	185
ii)	4-ABN-RCN	187
iii)	4-ABN-H ₂ O	190
iv)	4-ABN-CH ₃ OH	194
v)	4-ABN-CHCl ₃	194
4.3.3	Dispersed fluorescence spectra of the complexes	195
4.3.4	Fluorescence decay lifetimes	196
REFERENCES		206
CHAPTER 5: SPECTROSCOPY OF JET-COOLED AROMATIC AMINES		210
5.1	INTRODUCTION	210
5.1.1	N-inversion	210
5.1.2	Internal rotation of the CH ₃ group	211
5.2	EXPERIMENTAL	213
5.3	RESULTS AND DISCUSSION	213
5.3.1	Large amplitude motions of the amino group	213
i)	DMA	213
ii)	NMA	217
5.3.2	Spectroscopy of 2-ABN, 3-ABN, and 4-ABN	222
5.3.3	Fluorescence decay lifetimes of DMABN and 4-ABN	226
5.3.4	Van der Waals complexes of DMABN and 4-ABN	229
REFERENCES		235

LIST OF FIGURES

PAGE
NUMBER

CHAPTER 1:

1.1	Representation of solvent effects on the electronic transition energy of dipolar solutes in polar solvents. a) $\mu_g < \mu_e$ and b) $\mu_g > \mu_e$.	19
1.2	Fluorescence spectrum of DMABN in non-polar solvent (—) and in polar solvent (---).	23
1.3	Diagram of level-reversal brought about by solute-solvent reorganisation.	25
1.4	Schematic representation of TICT state formation.	28
1.5	Diagram of substituent induced level-reversal for 4-substituted dialkylanilines.	30
1.6	Some derivatives of DMABN.	31
1.7	Temperature dependent fluorescence spectrum of DMABN in n-butylchloride. Inset: Energy level diagram demonstrating TICT fluorescence from excited vibronic levels.	36
1.8	Kinetic scheme giving the parent-daughter relationship between the b^* and a^* states.	40
1.9	Selected compounds with TICT states.	43
1.10	Jablonski diagram illustrating the processes connecting the various electronic states.	50
1.11	Schematic of mixing of zero-order vibrational levels within a singlet electronic state.	53
1.12	Selected fundamental vibrations of benzene.	56

CHAPTER 2:

2.1	Schematic diagram of a free jet flow.	67
2.2	Diagram of the supersonic jet apparatus.	76
2.3	a) Oven nozzle assembly. b) Gas handling line.	77

2.4	Diagram of the expansion region.	79
2.5	Diagram of the apparatus used to measure fluorescence excitation spectra.	81
2.6	Potential energy diagram for the XeCl excimer.	84
2.7	Schematic of the electrical principle of the pulsed excimer system.	89
2.8	Schematic of the excimer laser gas system.	91
2.9	Diagram of the laser beam path through the dye laser.	93
2.10	Diagram of the laser beam path through the tuning block.	95
2.11	Diagram for the set up of second harmonic generation in the dye laser.	102
2.12	Circuit diagram of the dynode chain of the EMI XP2020 Q photomultiplier tube.	105
2.13	Diagram of the apparatus used to measure dispersed fluorescence spectra.	107
2.14	Diagram of the apparatus used to measure fluorescence decay lifetimes.	110
2.15	a) Diagram of a microchannel plate. b) Schematic representation of electron amplification of a single electron.	115

CHAPTER 3:

3.1	Possible modes active in the ground and excited states of DMABN.	126
3.2	Fluorescence excitation spectrum of DMABN. Two frequency progressions of 61cm^{-1} are indicated by ● and ▲.	128
3.3	Fluorescence excitation spectrum of N,N-dimethylaniline.	130
3.4	Dispersed fluorescence spectra of DMABN following excitation into: a) 0_0^0 , b) 61cm^{-1} and 99cm^{-1} modes.	134

3.5	Energy level diagrams to illustrate two possible assignments of the first member transition in the fluorescence excitation spectrum of DMABN.	136
3.6	Fluorescence decay curve for the 0_0^0 transition of DMABN.	140
3.7	Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for selected excited vibronic levels of DMABN.	141
3.8	Fluorescence excitation spectrum of the DMABN-methanol complex. a) The origin region. b) The 850cm^{-1} region.	144
3.9	Dispersed fluorescence spectrum of the DMABN-methanol complex following excitation of the 61cm^{-1} transition.	145
3.10	Charge distribution in the ground state and in the lowest electronic states for DMABN.	151

CHAPTER 4:

4.1	Theoretical calculations for ground and excited states of 4-ABN and DMABN.	158
4.2	a) Inversion vibration, ν_2 , of the NH_3 molecule. b) Potential energy curve for ν_2 of the NH_3 molecule.	161
4.3	The form of the vibrational wave function for an inversion vibration.	163
4.4	Vibronic transitions involving the NH_2 -inversion vibration in the $A^1B_2 \rightarrow X^1A_1$ system of the aniline molecule.	167
4.5	Transition dipole axes and inertial axis of 4-ABN.	168
4.6	Fluorescence excitation spectrum of 4-ABN. The inset shows the rotational contour of the 0_0^0 transition.	172
4.7	Dispersed fluorescence excitation spectra of 4-ABN following excitation into a) 0_0^0 , b) $6a_0^1$ (382cm^{-1}) and c) 1_0^1 (815cm^{-1}) modes.	176

4.8	Dispersed fluorescence excitation spectra of 4-ABN following excitation into a) $10b_0^2$ (493cm^{-1}) and b) I_0^2 (807cm^{-1}).	180
4.9	Fluorescence excitation spectra of a) 4-ABN- CHCl_3 , b) 4-ABN- H_2O and c) 4-ABN- CH_3OH complexes.	184
4.10	Rotational contours of the 0_0^0 transitions of a) 4-ABN, bare molecule and b) 4-ABN-Ar complex.	186
4.11	Rotational contours of the 0_0^0 transitions of a) 4-ABN- CH_3CN and b) 4-ABN- $\text{C}_3\text{H}_7\text{CN}$ complexes.	188
4.12	Rotational contours of the 4-ABN- H_2O excitation features occurring at a) 84cm^{-1} , b) 196cm^{-1} and c) 314cm^{-1} .	191
4.13	Schematic representation of MNDO optimised geometries of 4-ABN- H_2O complexes. In b), c) and d) the water molecule lies below the plane of the ring.	193
4.14	Dispersed fluorescence spectra of a) 4-ABN, bare molecule $\lambda_{\text{ex}} 0_0^0$ and b) 4-ABN- H_2O complex $\lambda_{\text{ex}} 84, 196$ and 314cm^{-1} .	196
4.15	Dispersed fluorescence spectra of 4-ABN- CH_3CN complex, $\lambda_{\text{ex}} 236\text{cm}^{-1}$.	197
4.16	Fluorescence decay curve for the 0_0^0 transition of 4-ABN.	201
4.17	Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for selected excited single vibronic levels of 4-ABN.	202
4.18	Fluorescence decay curve of the 4-ABN- CHCl_3 complex.	205

CHAPTER 5:

5.1	Fluorescence excitation spectra of a) NMA and b) DMA.	214
5.2	Fluorescence excitation spectra of a) DMABN, b) DMA and c) 4-ABN. Two frequency of 60cm^{-1} are indicated by $\bullet$ and $\blacklozenge$.	220
5.3	Fluorescence excitation spectra of a) 2-ABN, b) 3-ABN and 4-ABN.	224

- 5.4 Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for a) 4-ABN and b) DMABN. 227
- 5.5 Plot of frequency shift versus dipole moment for van der Waals complexes of 4-ABN and DMABN. 232

LIST OF TABLES

	PAGE NUMBER
CHAPTER 1:	
1.1 Frequency regions for selected normal vibrations of benzene derivatives.	57
CHAPTER 2:	
2.1 Typical experimental parameters for the measurement of fluorescence excitation spectra.	99
2.2 Operational parameters for the mode-locked ion pumped dye laser system.	113
2.3 Source of a) compounds and b) solvents used in this research.	117
CHAPTER 3:	
3.1 Calculated ground-state low-frequency normal modes of N,N-dimethylaniline and 4-N,N-dimethylaminobenzaldehyde.	131
3.2 Assignments and fluorescence lifetimes of the fluorescence excitation spectra of DMABN.	132
3.3 Assignments of the 0 ₀ ⁰ , 61 and 104cm ⁻¹ dispersed fluorescence spectra of DMABN.	137
3.4 Ground and excited state assignments of DMABN.	139
CHAPTER 4:	
4.1 Comparison of the frequencies of the optically active modes of 4-ABN with those of aniline, p-methylaniline and benzonitrile.	174
4.2 Assignments of the dispersed fluorescence spectra of 4-ABN.	178

4.3	Assignments of the dispersed fluorescence spectra, exciting into the $10b_0^2$ and I_0^2 modes.	181
4.4	Microscopic solvent shifts exhibited by 4-ABN van der Waals molecules.	183
4.5	Assignment of the dispersed fluorescence spectrum of the 4-ABN-acetonitrile complex, 0_0^0 excitation.	199
4.6	Fluorescence decay lifetimes of a) 4-ABN and b) 4-ABN complexes.	200

CHAPTER 5:

5.1	Assignments of DMABN, DMA, and NMA fluorescence excitation spectra.	216
5.2	Excited state assignments of the aromatic amines.	221
5.3	Ground state assignment of some of the large amplitude motions of DMABN and 4-ABN.	225

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

When electromagnetic radiation falls on a gaseous, liquid or solid material, which may be atomic or molecular in nature, the radiation may be transmitted, scattered or absorbed. It is the latter photophysical process, absorption, and the subsequent dissipation of energy by fluorescence which is fundamental to this thesis. Fluorescence is defined simply as the electric dipole transition from an excited to a lower electronic state, usually the ground state, of the same multiplicity. Most studies of fluorescence, absorption and other photophysical properties of aromatic molecules are made in the presence of a solvent medium. The observed spectral and photophysical parameters are characteristic of the molecule in its solvent environment rather than the isolated molecule as discussed below.

1.2 SOLVENT EFFECTS ON PHOTOPHYSICAL PROCESSES

When absorption spectra of aromatic molecules are measured in solvents of differing polarities, it is found that the position, intensity and shape of the absorption bands are modified by these solvents. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole and hydrogen-bonding)

which, above all, tends to alter the energy difference between the ground and excited states of the absorbing species. A qualitative interpretation of solvent shifts is possible by considering the momentary transition dipole moment present during absorption, the difference in permanent dipole moment between the ground and excited states of the solute [1-6], and the change in ground state dipole moment of the solute induced by the solvent and the Frank-Condon principle [1,7,8].

In the case of a dipolar aromatic molecule, if the solute dipole moment (μ) increases during the electronic transition ($\mu_g < \mu_e$), the Frank-Condon excited state is formed in a solvent cage of partly orientated dipoles. The better stabilisation of the excited state with increasing solvent polarity will result in a bathochromic shift. Its magnitude will be dependent on the extent of the change in the dipole moment during the transition, the value of the solvent dipole moment, and the extent of interaction between solute and solvent molecules (see figure 1.1(a)).

If the dipole moment of the solute decreases during the transition, the Frank-Condon excited state is a strained cage of orientated dipoles not correctly disposed to efficiently stabilise the excited state. Thus, with increasing solvent polarity, the energy of the ground state is lowered more than that of the excited state invoking a hypsochromic shift (figure 1.1(b))

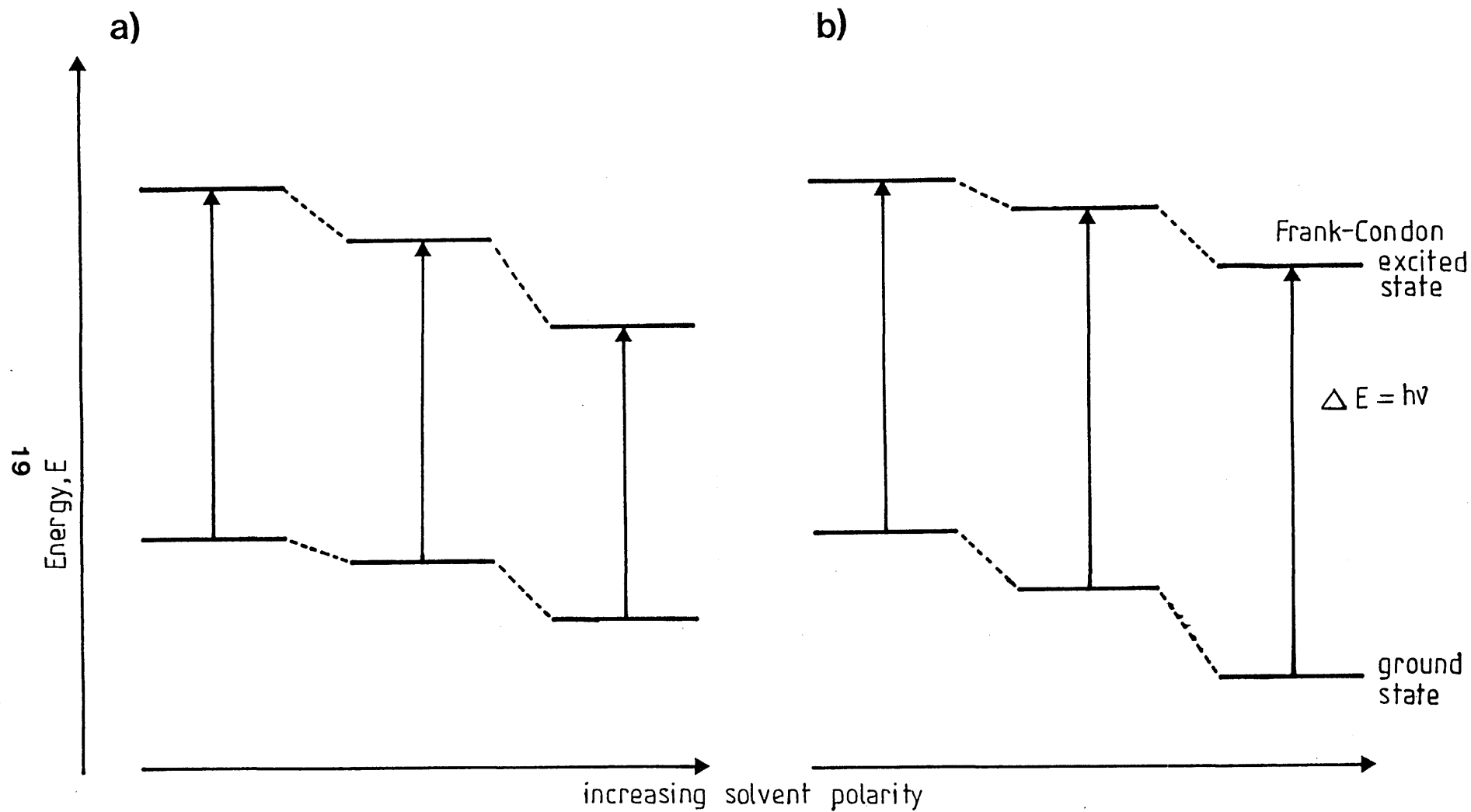


Figure 1.1 Representation of solvent effects on the electronic transition energy of dipolar solutes in polar solvents.

a) $u_g < u_e$ and b) $u_g > u_e$.

The studies of medium effects on excited state dynamics, whether they are in solution, matrix or solid form, considers a broad spectrum of photophysical phenomena. Included among them are solvent effects on radiative lifetimes [9], solvent-induced electronic relaxation in molecules corresponding to the intermediate level structure [10], solvent perturbations of electronic relaxation in molecules, which correspond to the statistical limit [10] and medium-induced vibronic relaxation [11]. The information that can be obtained from these studies is inherently limited for several reasons:

1) The accumulative affects exerted by the solvent on the solute consist of a superposition of individual pair (or higher order) contributions from distinct solvent species (coordination or solvation number).

2) Solute-solvent interactions are determined by local structure of the solvent around the solute.

3) The solute-solvent interactions may be complicated by dynamic motion of the solvent.

Hence, information regarding the effects of intermolecular interactions on energetics and intramolecular dynamics cannot be readily resolved from traditional experimental data on solvent perturbation in a dense medium [12].

1.2.1 Specific solute-solvent interactions

So far, only bulk solute-solvent effects have been considered. Spectral changes which arise from alteration of the chemical nature of the chromophore by the medium such as proton or charge-transfer between solvent and solute, solvent dependent aggregation, ionisation, complexation or isomerisation equilibria have not been discussed. Many recent investigations have concentrated on the role of the solvent in the charge-transfer process for molecules in solution [13-20]. Both intramolecular [15,16] and intermolecular [17] charge separations have been studied. The solute-solvent interactions can be passive, as observed in the cage effect where the primary role of the solvent is to trap the solute particles within a volume enabling them to collide and react with each other [18]. The solute can also be actively coupled with the medium, as in the case of charge-transfer reactions where the energies of initial, intermediate and final states, the reaction pathways leading to different products, and the kinetics of the transitions can be dramatically affected by the solvent. Static [19] and dynamic [20] polarity effects as well as local solute-solvent interactions [21] such as hydrogen bonding are important in these latter processes.

4-N,N-dimethyl aminobenzonitrile (DMABN) provides an interesting example of a molecule that interacts strongly with polar solvents, as discussed overleaf.

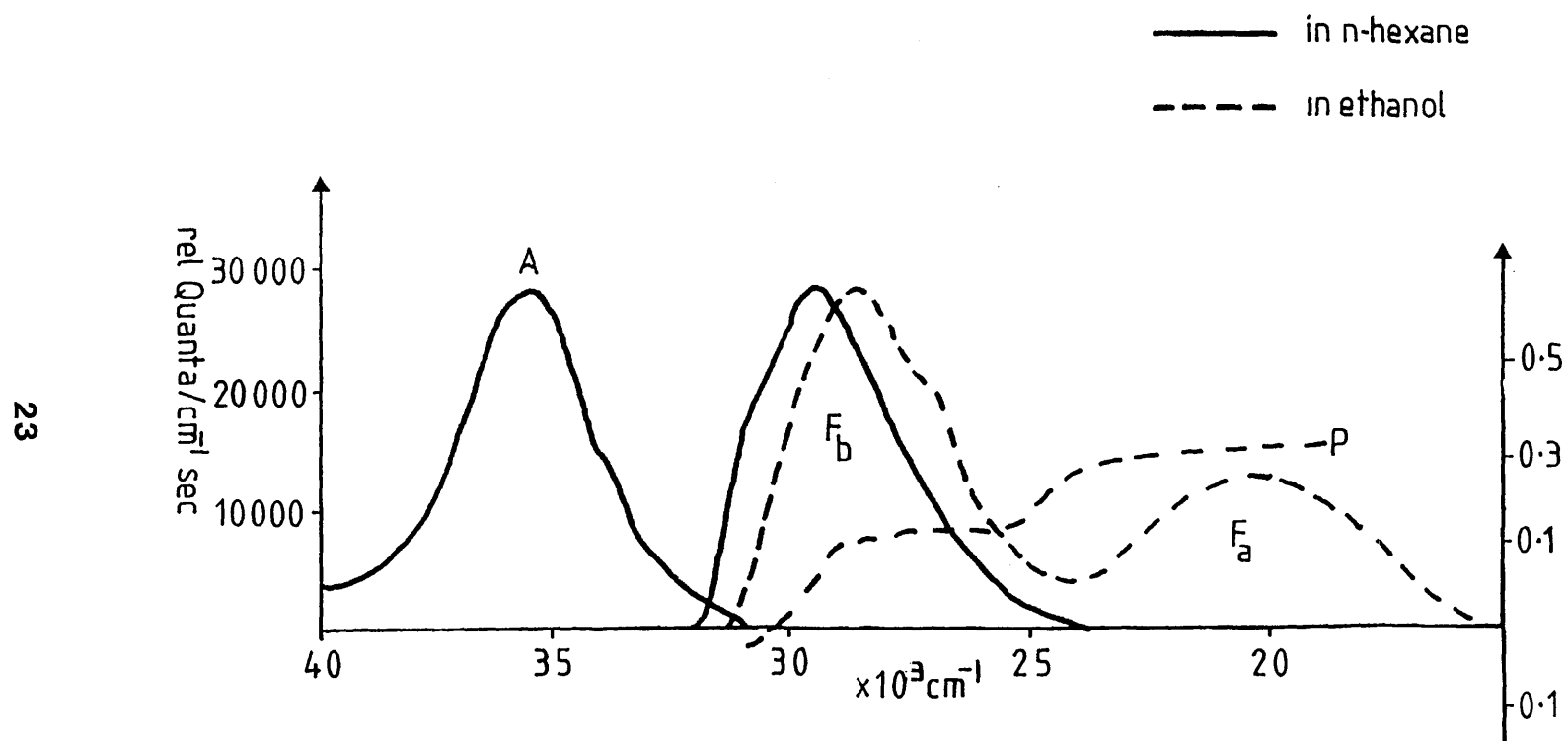
1.3 THE ANOMALOUS FLUORESCENCE BEHAVIOUR OF DMABN

1.3.1 The observation of dual fluorescence

Over 25 years ago, Lippert et al [22] discovered that a simple benzene derivative, DMABN exhibited unusual fluorescence properties in polar solutions. In a non-polar solution DMABN emits "normal" fluorescence related to that given by other similar benzene derivatives. In polar solutions, besides the normal fluorescence, there is an anomalous red-shifted emission. This is illustrated in figure 1.2 [23]. These two fluorescence bands were assigned by Lippert et al to be the b-band (b^* fluorescence) for the normal short wavelength ${}^1L_b$ -type emission and a-band (a^* fluorescence) for the anomalous ${}^1L_a$ -type emission. The subscripts "a" and "b" refer to the direction of polarisation, the b-band being polarised along the short axis in a transverse polarisation and the a-band along the long axis. This is known as Platts notation and is derived from the perimeter free electron orbital model (PFEOM) [9].

The maximum for the b^* emission is approximately 350 nm and that of the a^* emission is solvent dependent and ranges from 420-500 nm [22]. Since the discovery of this phenomenon, a great deal of interest has been demonstrated in DMABN and similar molecules. Much controversy has surrounded the kinetics of formation of

Figure 1.2 Fluorescence spectrum of DMABN in non-polar solvent (—) and in polar solvent (-----).



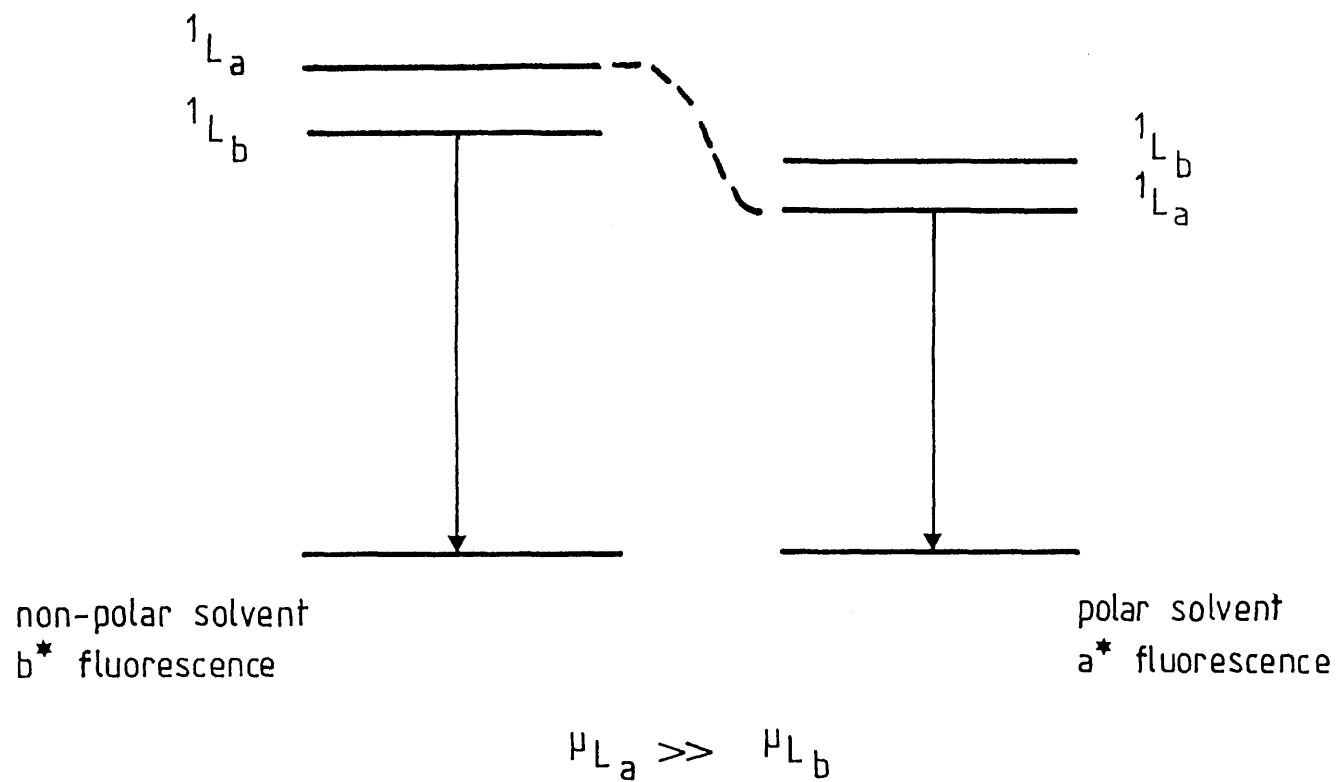
Absorption, A, and fluorescence, F, of DMABN in n-hexane at room temperature and dual fluorescence and fluorescence polarisation energy, P, (excitation energy indicated by arrow) in ethanol at 140K.

these states and various mechanisms have been proposed for the dual fluorescence as discussed below.

Lippert et al [22] had assigned the states ^1L_b (less polar) and ^1L_a (strongly polar) which were said to undergo level reversal brought about by solute-solvent reorganisation (see figure 1.3). The ^1L_a state lies above the ^1L_b state in free molecules, but these states do lie close to each other. In fluid solutions at room temperature, the solvent molecules surrounding the excited DMABN molecule will generally have time to reorientate themselves before light emission occurs and hence they relax to their preferred equilibrium configuration which is of lower energy.

In non-polar solvents, the ^1L_a states of these molecules still lie above ^1L_b even in the preferred equilibrium configuration and hence fluorescence occurs from the ^1L_b state. In polar solvents, the interaction between dipole moments of the excited DMABN and solvent molecules lowers the energy of the ^1L_a state below that of ^1L_b in their equilibrium configuration and hence fluorescence occurs from the ^1L_a state [24]. If this were the case, then the transition moments to these states should lie in the molecular plane perpendicular to one another. This model was later discounted by the observation made by Rotkiewicz et al [25] of parallel polarisation along the long axis of the molecule, for both bands, using glycerol as a solvent. They attributed

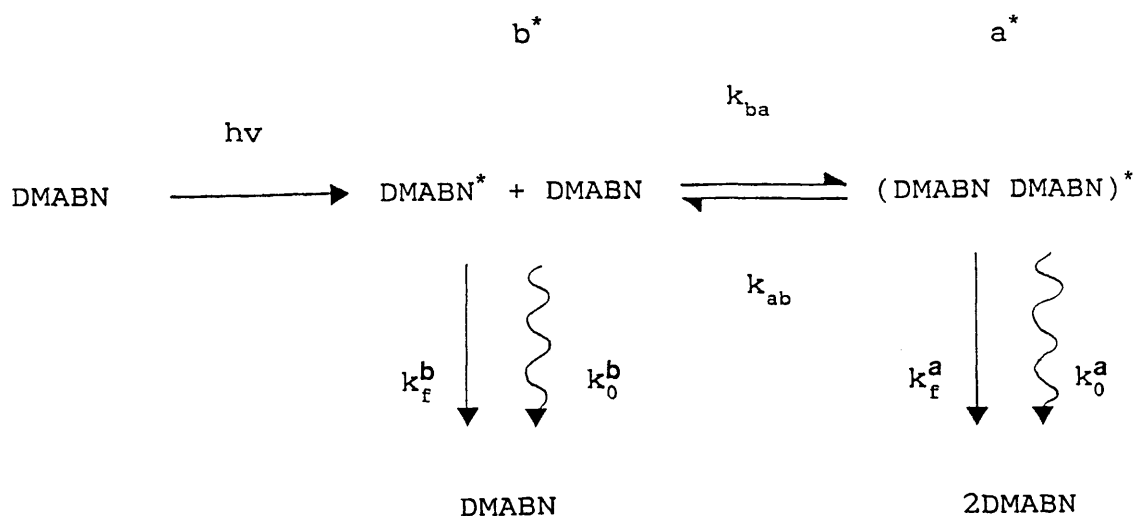
Figure 1.3 Diagram of level-reversal brought about by solute-solvent reorganisation.



the b^* and a^* emission to two excited species differing in the polarity and orientation of the amino group: a lone electron pair either parallel or perpendicular to the plane of the benzene ring. Conversely, in ethanol [23], the fluorescence polarisation for the a - and b -bands is dissimilar, suggesting that the b -band in ethanol derives from a different state to that in glycerol (see figure 1.2). The b -band in glycerol is in fact being derived from the ${}^1L_a$ type state of the planar molecule which is lower in energy than the ${}^1L_b$ type. The contrary results obtained with ethanol and other lower alcohols are discussed in detail on page 37.

Excimer formation was proposed as an explanation of a^* fluorescence by Khalil et al [26,27]. This involves the association of two DMABN molecules to form a dimer which is bound in the excited state but dissociated in the ground state. See scheme 1 below:

SCHEME 1.



see page 34, scheme 2 for the definition of k .

There was no observed concentration dependence of the intensity ratio of the bands, as expected for excimer formation, and so there was little support for the theory.

Kosower and Doduik [28] suggested that intermolecular excited state proton transfer was occurring but the observation of the dual fluorescence in pure aprotic solvents had already been seen [22].

One of the most experimentally confirmed mechanisms was initially proposed by Grabowski et al [29]: the formation of a twisted intramolecular charge transfer state (TICT).

1.3.2 The TICT state hypothesis

Grabowski et al proposed that the b^* emission arises from a planar state and the a^* emission from a highly polar twisted state. The formation of the a^* state occurs via a dynamic relaxation of DMABN with internal twisting of the dimethylamino group coupled with electron transfer from the amino nitrogen to the π^* orbital extending over the whole benzonitrile group (see figure 1.4). The proposal was initially based on fluorescence polarisation measurements carried out in glycerol, as mentioned previously, which gave the same polarisation along the axis connecting the amino and cyano groups for both transition moments. This is a

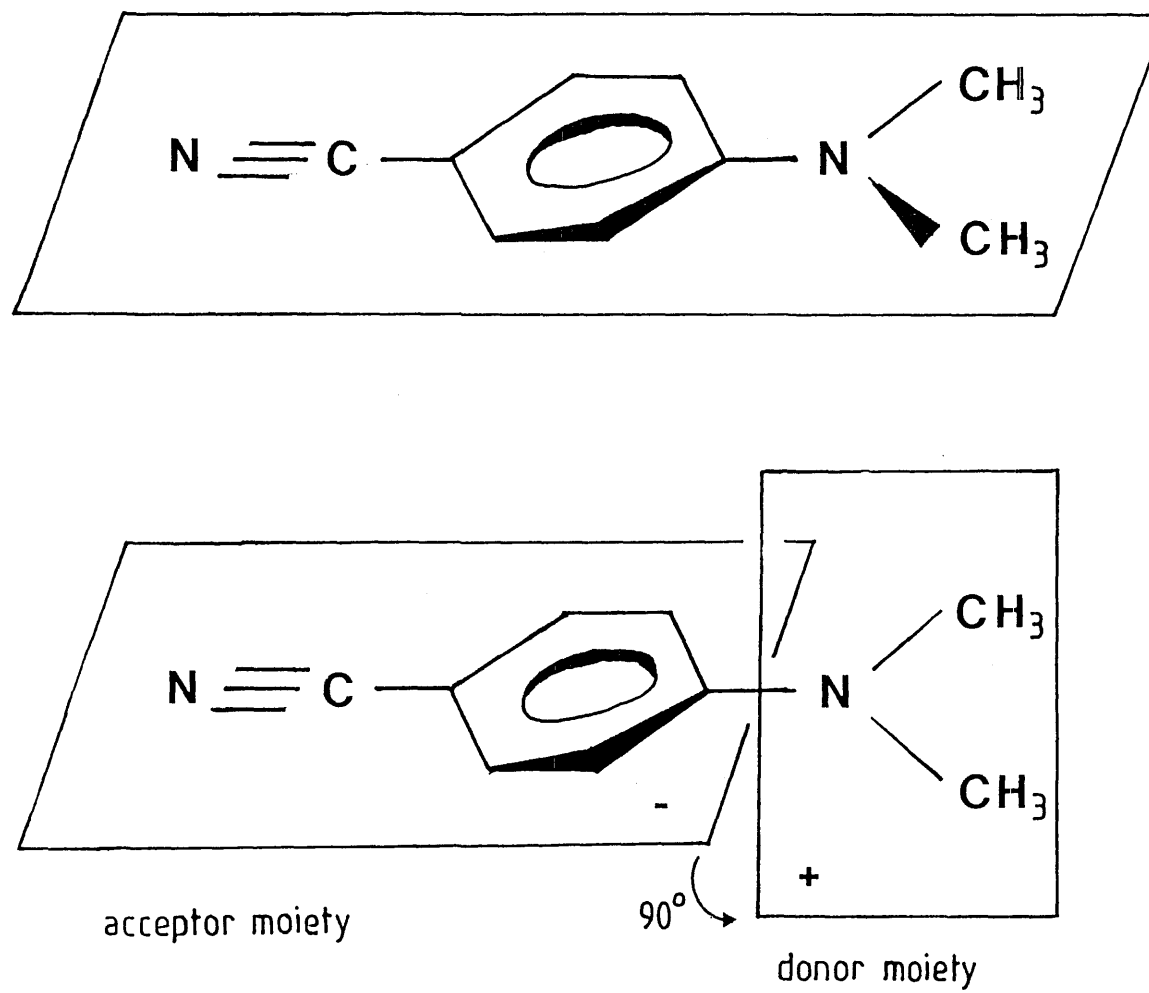
polar
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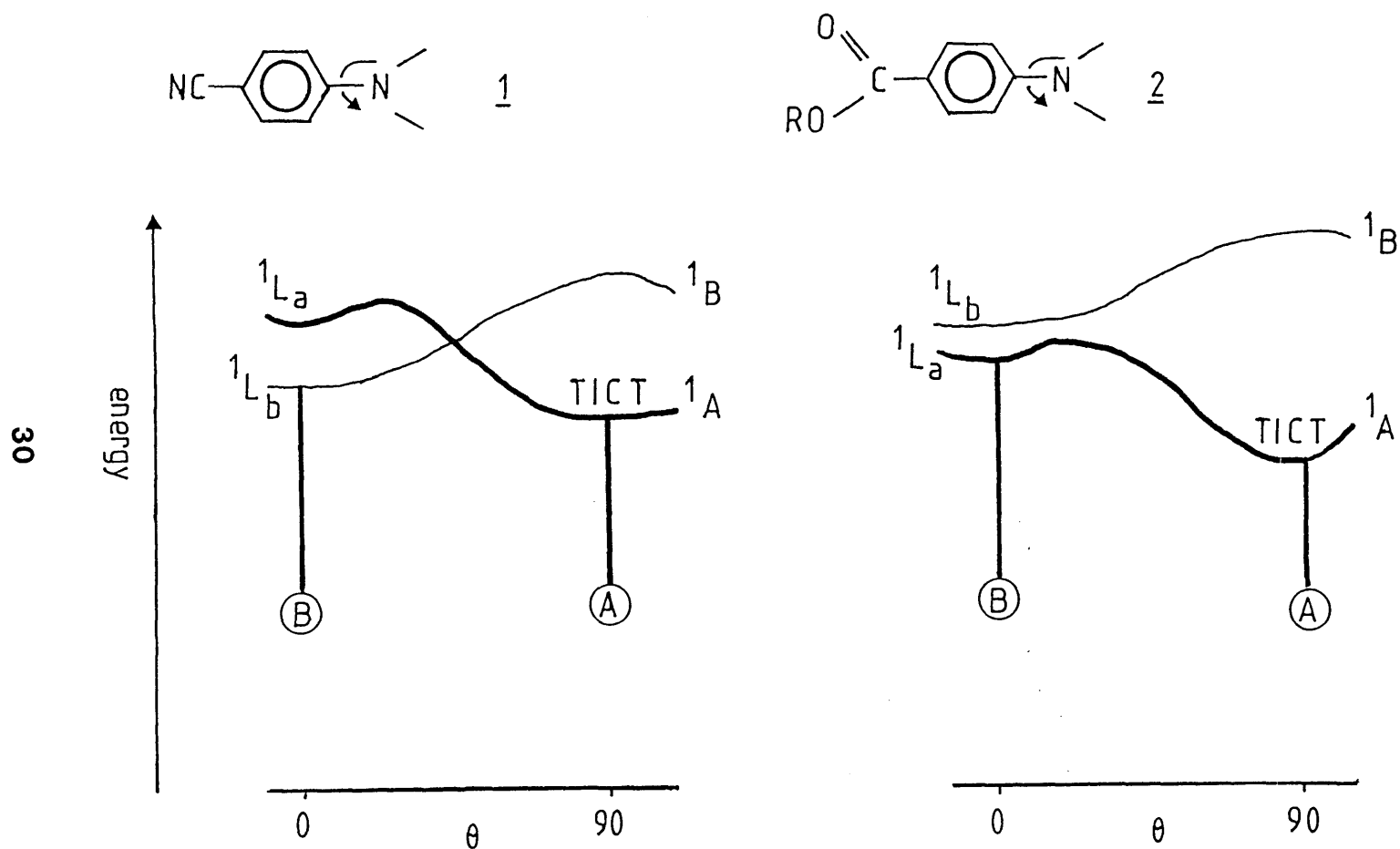
Figure 1.4 Schematic representation of TICT state formation.

solvent induced level reversal. Similarly, substituent induced level reversal can be obtained.

From figure 1.5 the substituent level reversal for p-cyanoalkylaniline can be discerned. On progressing from the cyano to the alkoxy carbonyl derivatives (a stronger acceptor group) the ^1L_b -state is shifted to higher energy and the ^1L_a -type state to lower energies. Because both the ^1L_a and TICT states are of a symmetry species A (C_2 point group), they correlate without crossing for the alkoxy carbonyl derivatives and with excited state crossing for the cyano derivatives [23]. The substituent level reversal can be followed by fluorescence polarisation or radiative decay rate constant measurements due to the resulting change in the nature of the b^* fluorescence.

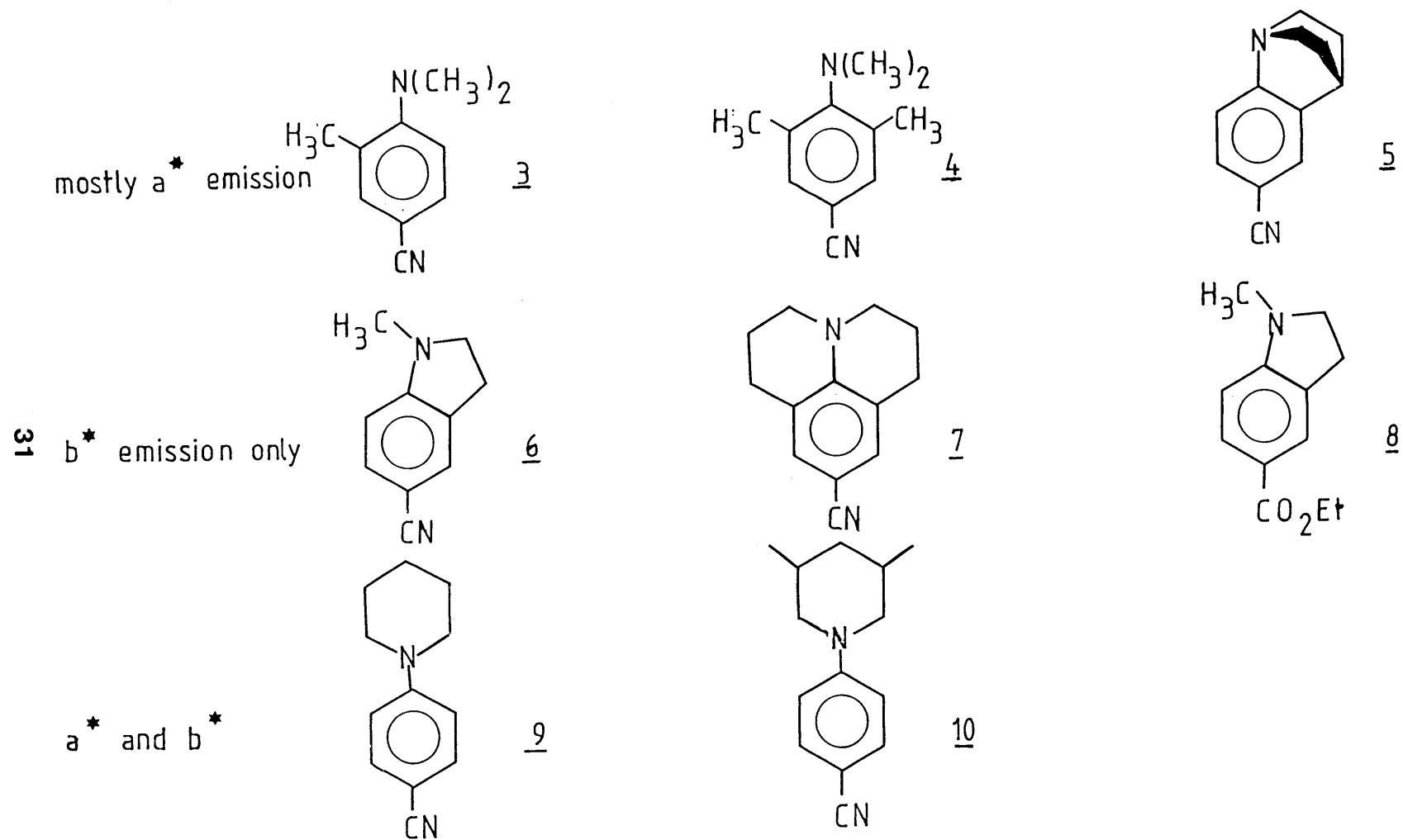
From figure 1.4 it can be seen that a steric hindrance to the coplanarity of the amino group and the ring will give a twisted structure and so should favour TICT formation. Indeed, further proof for the TICT hypothesis was obtained by synthesising model compounds of DMABN that either held the amino group rigidly in the planar or perpendicular position [29-33]. In figure 1.6, sterically hindered ortho- CH_3 derivatives of DMABN, 3 and 4 emit preferentially or only the a^* fluorescence due to the CH_3 group forcing the amino moiety out of plane of the benzene ring. More convincingly, compounds 6, 7 and 8, which are held

Figure 1.5 Diagram of substituent induced level-reversal for 4-substituted dialkylanilines.



On going from the cyano to the alkoxy-carbonyl derivatives the ${}^1L_b$ -type state is shifted to higher energy and the ${}^1L_a$ state to lower energy.

Figure 1.6 Some derivatives of DMABN.



rigidly planar, emit only the b-band. Comparing these with compound 5, where the lone electron pair on the nitrogen atom is lying in the plane of the ring orthogonal to the π -orbitals, only the a-band is emissive.

A different approach was to compare the dynamics of intramolecular twisting for donor groups of varying molecular weights [29,31,34]. At room temperature where the thermodynamic equilibrium, $a^* \rightleftharpoons b^*$ is established within the lifetime of the excited state [35], the dual fluorescence of 9 and 10 are almost identical. At lower temperatures, the relative intensity of TICT fluorescence of 10 is decreased considerably. This is thought to indicate slower formation of a^* in 10 compared with 9 due to the greater molecular weight of the amino moiety.

TICT emission has been observed in the gas phase for 2 [36,37] and for a series of N-phenyl pyrrole derivatives [38,39]. In each case, due to steric factors, the amino group is already strongly twisted in the ground state.

Recent $S_n \leftarrow S_1$ picosecond transient absorption studies [40,41] have been carried out with DMABN and like-molecules. Okada et al [40] observed that the $S_n \leftarrow S_1$ absorption spectrum of DMABN in acetonitrile solution was essentially the same as that

for 2,3,5,6-tetramethyl-4-N,N-dimethylaniline benzonitrile (HMABN) which in turn is very similar to the absorption spectrum of the benzonitrile anion radical. The amino group in HMABN is already twisted out of plane in the ground state. Also, the $S_n \leftarrow S_1$ absorption spectra of DMABN in medium polar solvents such as ethyl ether and dioxane are well produced by the superposition of the absorption spectrum in non-polar solvent, cyclohexane, and that in polar solvent, acetonitrile. From their observation they concluded that:

1) The electronic structure of the TICT state maybe represented by a full charge transfer from the amino group to the benzonitrile moiety.

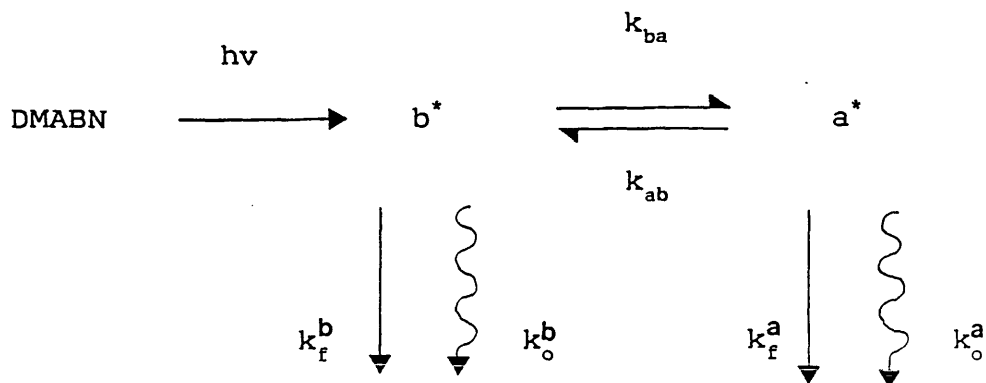
2) The reorientated relaxation of the polar solvent molecules induces twisting in the excited state of DMABN leading to the formation of the TICT structure.

Hence, they were in agreement with the TICT state mechanism as proposed by Grabowski et al [29]. Rulliere et al [41] made similar conclusions from their picosecond absorption spectra of carbonyl derivatives of dimethylaniline and supported the observation of Otaga et al [40].

1.3.3 Kinetics of the TICT state

The kinetics of formation of the TICT state are summarised in scheme 2.

SCHEME 2



k_{ba} = forward reaction rate constant

k_{ab} = backward reaction rate constant

k_f = radiative decay rate to ground state

k_o = non-radiative decay rate to ground state

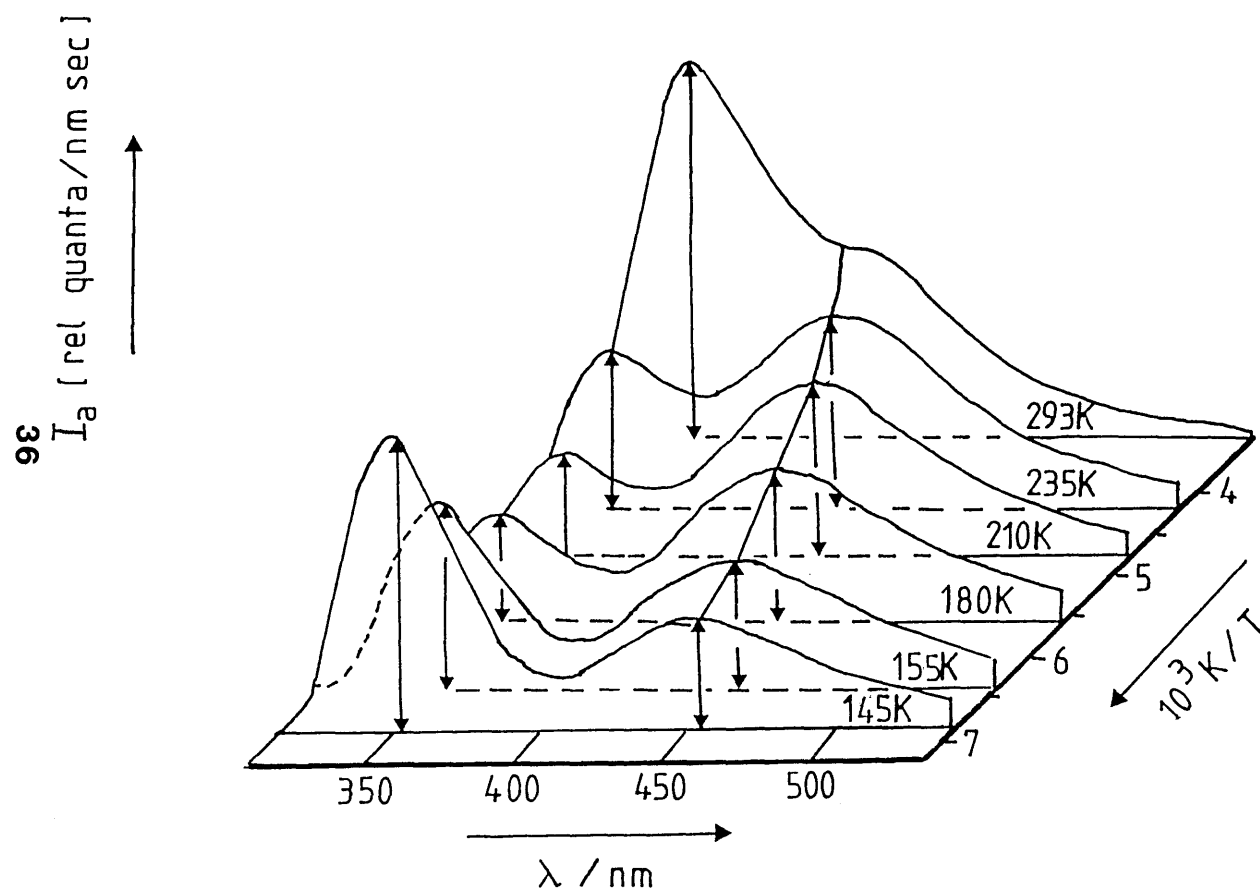
The scheme is similar to that for excimer formation but in order to explain the experimental observations three temperature dependent rate constants (k_{ba} , k_{ab} and k_f^a) are required.

The proposed precursor product relationship of the b^* and a^* states is experimentally supported by numerous nanosecond and picosecond studies [42,43-50]. These show that for the irreversible case (k_{ab} negligible), that the a^* fluorescence builds up with a rise time that is related to the decay time of the b^* fluorescence. Both solvent (viscosity and polarity) and solute parameters (structural: ground state twist angle, rotating volumes, molecular shape and flexibility; electronic: state correlation and conical intersections)

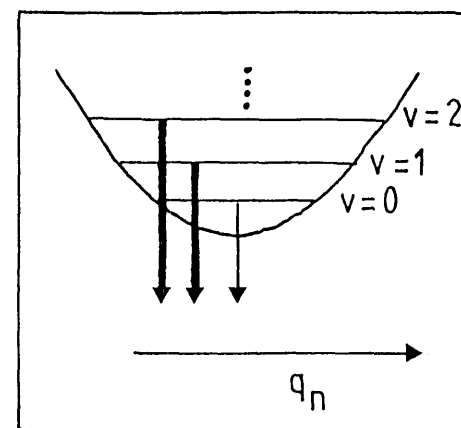
determine the rate constant k_{ba} for the formation of the TICT state. The characteristic intensity minimum for the shorter wavelength b-band occurs at the temperature above which the excited b^* and a^* states reach a thermodynamic equilibrium during their nanosecond lifetime (see figure 1.7). Upon increasing the temperature [39] the equilibrium shifts towards b^* resulting in an increase of the total fluorescence quantum yield because the deactivation of a^* , unlike that of b^* , occurs mainly via non-radiative processes (see figure 1.7). The slight increase of quantum yield of a^* with temperature is due to the forbidden nature of the radiative process and is termed "hot fluorescence". Because the radiative transition, $a^* \longrightarrow$ ground state (a back charge transfer transition) involves orbitals perpendicular to one another, the transition, on average, is overlap forbidden and thus expected to possess a small transition moment. A small TICT fluorescence quantum yield would therefore be expected. However, by coupling to suitable vibrations, this transition can borrow intensity from higher-excited, more allowed states which accounts for the appreciable quantum yields. The fact that the rate constant for the radiative decay of TICT states increases with temperature and that, therefore, a temperature dependent fluorescence rate constant k_f^a is required for scheme 2 is in accordance with this picture of vibronic coupling. Hence the major proportion of observed TICT fluorescence is emitted from higher

Figure 1.7 Temperature dependent fluorescence spectrum of DMABN in n-butylchloride.

Inset: Energy level diagram demonstrating TICT fluorescence from excited vibronic levels.



inset



vibronic levels (see figure 1.7 (inset)) and can be termed "hot fluorescence".

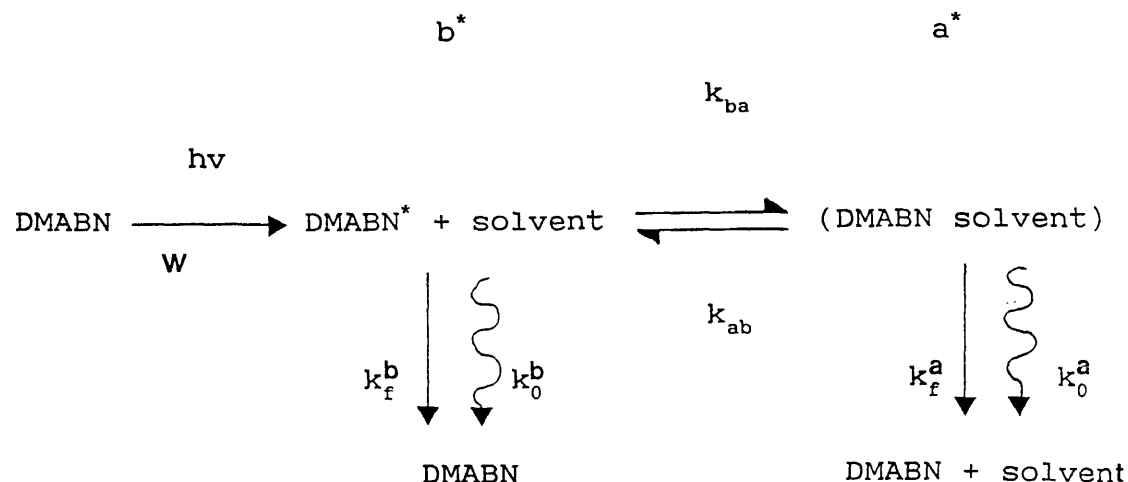
1.3.4 The role of specific solute-solvent interactions

The majority of studies of DMABN and like molecules have been carried out in the solution phase where specific solute-solvent interactions may take place. Some mechanisms which invoke such interactions have been proposed and subsequently discounted, as discussed earlier. There are still two such mechanisms which, although they do not replace the TICT mechanism, do supplement it.

(i) Exciplex formation

Chandross [51] provided evidence of the formation of an emissive exciplex. An exciplex (excited complex) is a complex of definite stoichiometry that is associated in an electronic excited state but dissociated in the ground electronic state. The term exciplex is restricted to an excited complex of definite stoichiometry, which may differ from 1:1 in some cases, to distinguish it from the case of a solvated excited molecule interacting with an indefinite number of unexcited molecules forming its solvent environment [52]. The mechanism for the formation of an exciplex is shown overleaf in scheme 3.

SCHEME 3



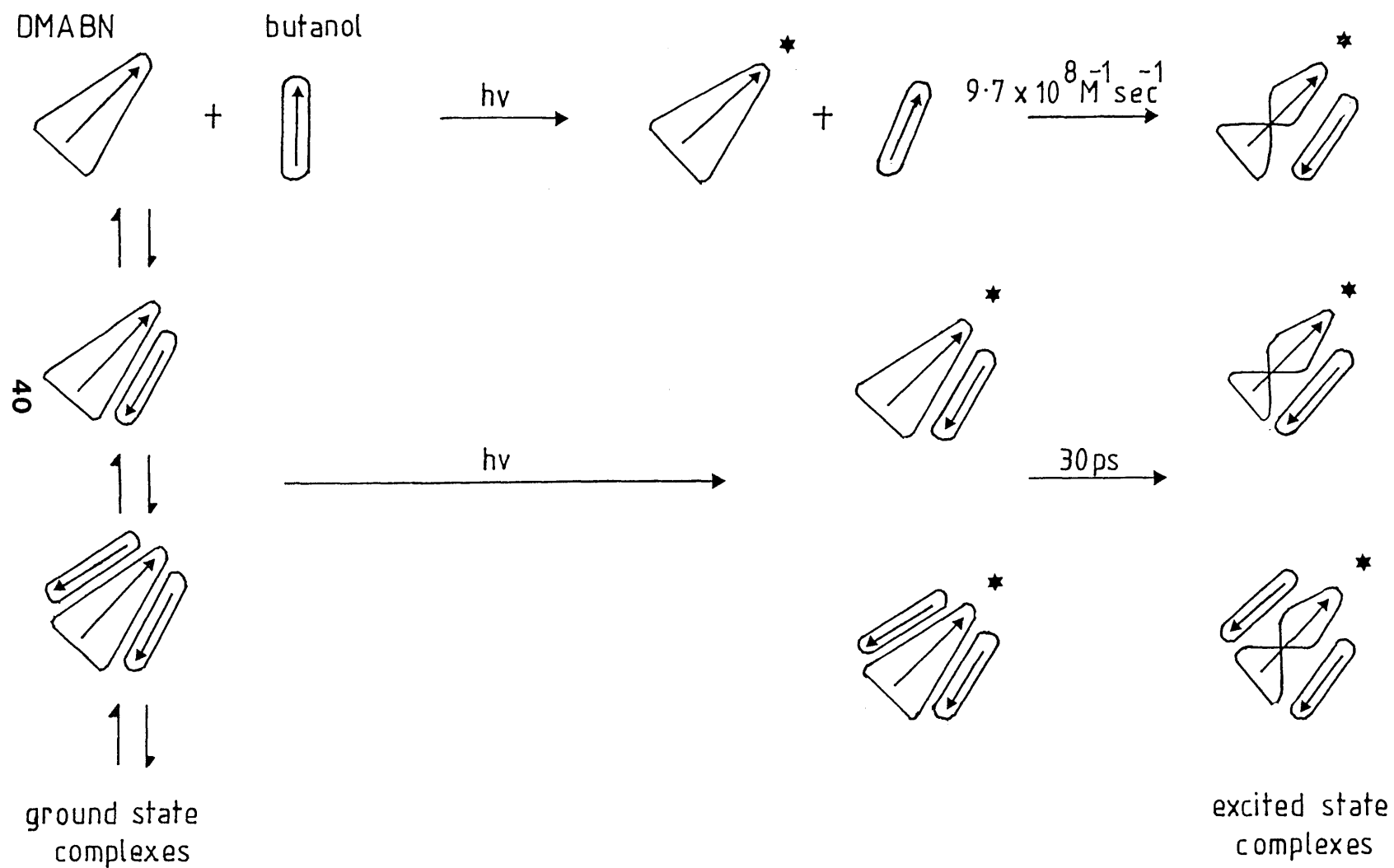
Exciplex formation involves the association of a polar solvent molecule with a molecule of DMABN in its excited state. This mechanism has received much support by Visser, Varma et al in recent years [43,53-56]. Wang and Eisenthal [16] attributed the anomalous long wavelength emission to a complex formed between excited DMABN and butan-1-ol with a rate constant of $9.7 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$ which is too slow for a diffusion controlled interaction. There were three key observations:

- 1) The appearance of a fast and slow decay component upon the dilution of the butanol solutions with non-polar solvent.
- 2) The dynamics of the observed fast process was independent of the dilution while the slow process showed a linear dependence on the butanol concentration.
- 3) The fast process dominates at high concentrations.

The origin of the fast process (30 ps rise for propan-1-ol, for all concentrations) was attributed to the excitation of complexes formed in the ground state between DMABN and butan-1-ol (see figure 1.8). The formation of the ground state complexes not being unexpected due to the large dipole moment of DMABN, 7D, [29] (the experimental importance of the formation of these ground state complexes to the project will be explained later). Hence, the short rise time is mainly due to the intramolecular bond twisting motion along the C-N(CH₃)₂ bond of the excited DMABN complex. The details of the ground state complex whether 1:1 or 1:n appeared not to be critical to TICT formation as shown in figure 1.8. The slow component rise observed was thought to be due to the excitation of DMABN molecules which either did not have or had the wrong orientation of butan-1-ol molecules (see figure 1.8). The dominant stabilisation of the TICT state was concluded to be due to a short range specific interaction with a polar solvent molecule.

A secondary solvent effect arises from further stabilisation of the complex by long range polarisation interaction with solvent molecules. Wang and Eisenthal [16] had demonstrated a parent-daughter relationship between the a* and b* emitting states, these states reaching rapid equilibrium upon excitation. The short lived component was also observed by Meech and Phillips [44] in ethanol. The viscosity dependence of the

Figure 1.8 Kinetic scheme giving the parent-daughter relationship between the b^* and a^* states.



transformation rate, which decreases as the solvent viscosity increases, was consistent with the interpretation that bond twisting and solvent reorganisation are involved. Bonding between the components of the exciplex is attributed to the overlap of the lone pair orbitals on the solvent molecule and on the amino group [53]. This type of specific solute-solvent interaction may actually take place for lower alcohols but is not thought to be a general case for TICT emission [38] because

1) Some molecules exhibit TICT fluorescence in the gas phase.

2) The alkoxy carbonyl and the cyano-substituted dialkylanilines have fluorescence spectra in polar solvents that are similar.

3) The alkoxy carbonyl substituted derivatives show TICT emission in aliphatic hydrocarbons where no specific interactions are possible.

Wang [57] agreed with the above points after his experimental observations for DMABN in a series of alkylnitriles supported the TICT mechanism.

ii) 3-electron sigma bonding

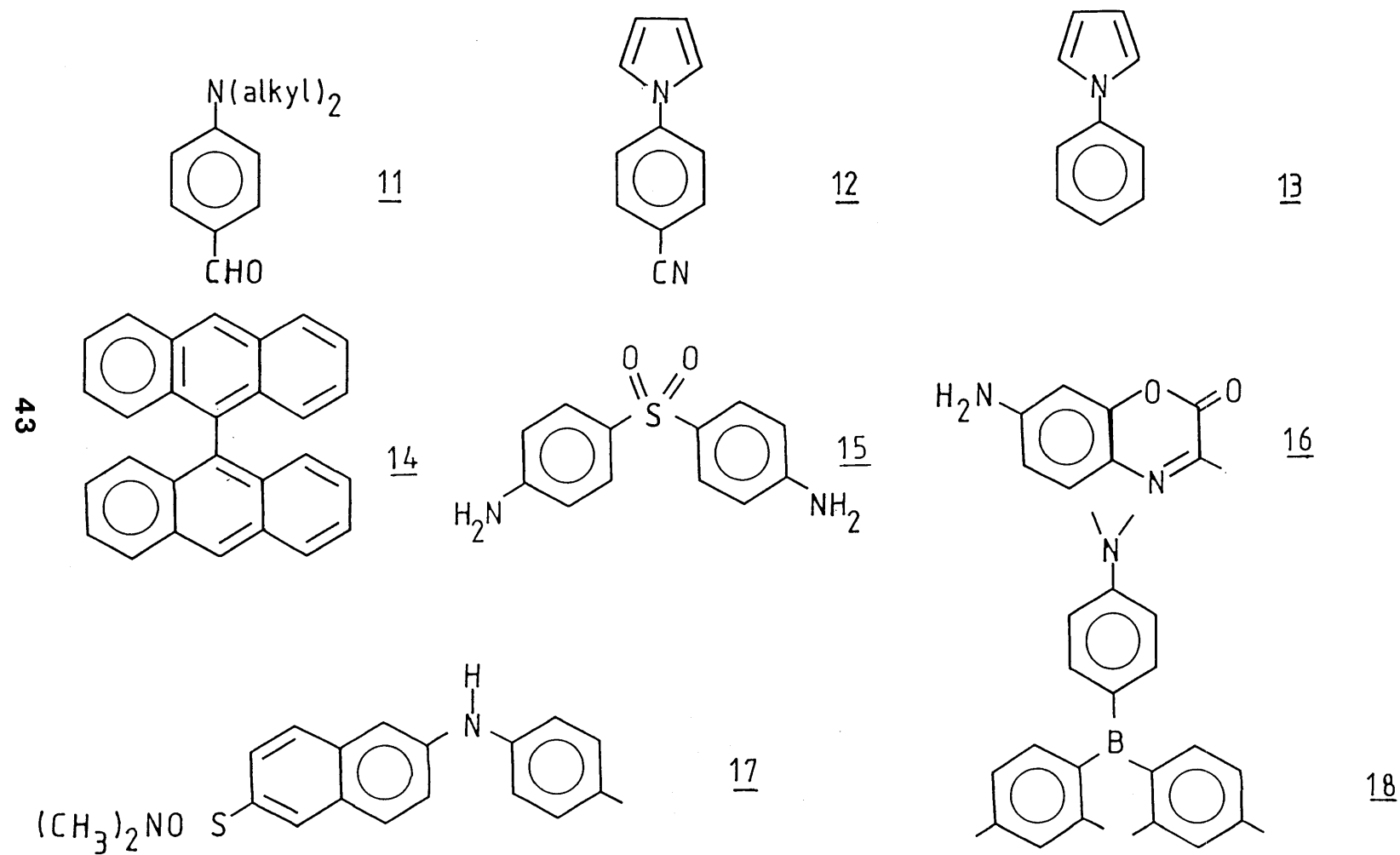
More recently Wang [57] observed the quenching of a^* emission by tertiary amines. The quenching rate was not controlled by the oxidation potentials of the

amines but by the size of the amine alkyl group. This unusual steric effect indicates a short range interaction which was attributed to a three electron sigma bonding mechanisms between the two nitrogen atoms $[-\text{ArylMe}_2\text{N} : \text{NR}_3]$, although there was an absence of initial decay components as observed in alcohols. Normally the interaction between nitrogen lone pair electrons of two neutral amines is destabilising, but stabilising when one of the amines is oxidised to a radical cation due to the formation of a three electron bond. Hub et al [58] proposed that the three electron sigma-bonding mechanism is responsible for the quenching of intermolecular exciplex at high amine concentration observed in many systems. In these cases, the first amine molecule is virtually "oxidised" upon the formation of the exciplex which then facilitates the interaction with a second amine molecule to form a triplex where the donor is a diamine radical cation. Though this is applied to trans-stilbene, Wang [57] suggested the interaction between the a^* emission and the amine should also be governed by the three sigma bonded electron mechanism.

1.3.5 Other compounds with TICT states

So far, this discussion has been limited to DMABN and its closely related derivatives. There are numerous other compounds which will form TICT states, emissive and non-emissive, [29,59-62] a selection of which are shown in figure 1.9. For a more extensive list

Figure 1.9 Selected compounds with TICT states.



see Rettig's comprehensive review of TICT compounds [38].

Of the three types of compounds 1, 2 and 11, 2 exhibits the strongest TICT emission because the conical intersection is absent (see figure 1.5) and the $n\pi^*$ states are high in energy and do not lead to fast non-radiative decay as in 11. By using a stronger donor group, for example, a pyrrole ring as in 12, even the parent compound, 13, shows dual fluorescence. The biaryls, 14, are unusual in that they are non-polar and highly symmetric in the ground state and yet form a very polar TICT state upon excitation.

Diphenylmethane dyes, such as Michlers ketone (bis(4-aminophenyl)sulfone), 15, also exhibit multiple fluorescence. Picosecond studies [60] reveal that for longer chain alcohol solvents (ethanol to hexanol) wavelength dependent rise times were observed and longer rise times with decreasing emission energy. Multiple decay components were observed for wavelengths higher than the TICT emission maximum (λ^{TICT}) and only red edge ($\lambda > \lambda^{\text{TICT}}$) revealed rises and decays of single exponentials. These observed kinetics were interpreted in terms of solvent reorganisation in order to stabilise the charge-separated state. The strong TICT fluorescence is possibly due to p_{π} - d_{π} interaction at the sulphur atom [38].

Not all TICT states are emissive. Laser dyes such as coumarins 16 [62] are strongly affected in their

photophysical properties by a solvent polarity dependent decay towards a non-emissive TICT state. In this case the decay is so pronounced that even in saturated hydrocarbon solvents or in an ethanol matrix at 77 K all the excited molecules decay via the TICT state which is identified by its weak emissive properties.

Another class of compound giving emissive TICT state is 17 [62]. 17 and like molecules have been used extensively as fluorescent probes in biological systems. They decay by rotation of the aniline group around the N-naphthyl bond leading to an emissive TICT state.

The range of TICT compounds is not limited to strictly organic compounds. Some of the unusual fluorescence features in silicon, boron organometallic 18 compounds can be attributed to the formation of a TICT state [38].

1.3.6 Conclusion for DMABN

The results that have been accumulated for DMABN indicate that both bond twisting (between the amino group and the benzene ring) and solvation play an important part in the charge distribution. But in spite of the numerous studies on the subject, the relationship between the two fluorescence bands is not fully understood. The mechanism by which the solvent molecules stabilise the intramolecular charge transfer is not clear, that is, whether long range polarisation

interactions are in play or whether there are local solute-solvent interactions. In the latter case which has been shown experimentally to occur for DMABN in lower alcohols (ethanol to butanol) [16], the number of solvent molecules involved in the process is still unclear.

An experimental method which can overcome the problems encountered in solution phase is the study of the molecule in a van der Waals complex formed in a supersonic jet as discussed below. The prerequisite for this being the formation of a ground state complex. Because there is the presence of a rapid rise component [16] which indicates the formation of ground state complexes (in this case butanol), it therefore could be expected that the a^* fluorescence could be formed and observed under supersonic jet conditions.

1.4 VAN DER WAALS MOLECULES

Van der Waals (vdW) [65,66] molecules are weakly bound molecular complexes held together by attractive interactions (for example, dispersive, electrostatic, hydrogen bonding and charge transfer) between closed shell atoms or molecules. The primary characteristics of a vdW complex being the low dissociation energies ($10-1000\text{ cm}^{-1}$), the long bond length and the retention of many of the individual properties of the molecular constituents [65].

Consequently, a vdW complex of a diatomic or polyatomic molecule and simple ligands such as rare gas atoms can be viewed as a molecule in a characterised local solvent configuration, the excited state features of which can be studied in a supersonic jet (see chapter 2).

The first studies of vdW complexes carried out in a supersonic jet were those for iodine with helium [67] and neon [68]. The information obtained included the photoinduced vibrational predissociation of the B state being observed and structure, fluorescence decay lifetimes, binding energies, quantum sharing rules and product state distributions were determined for these vdW complexes.

Supersonic expansions prove useful for the study of these vdW complexes in order to determine ground state structure and energetics, the excited state energetics as well as the dynamics of the predissociation of a vdW complex. All the information obtained on these vdW complexes contributed towards the understanding of solvent perturbations from the microscopic point of view. Subsequent work on weakly bound complexes involved aromatic species and rare gases such as Ne and Ar [65,69-72]. Progress was then made to complexing agents with higher molecular weight (methane, chloroform, water, methanol, benzene and toluene) with aromatics such as tetracene and fluorene [73].

Work by Haynam et al [74] successfully identified two different isomers of the dimer of s-tetrazine while more recently Slaw et al [75] reported the findings on various combinations of benzene and toluene molecules. Doxtader et al [76] reported on complexes of benzene with perylene and anthracene. In general, the principal vibronic modes of the complexes correspond to those of the uncomplexed parent molecule and features observed in the excitation are normally red-shifted from the origin of the spectrum [76].

Over the last few years the technique has been applied to the observation of intermolecular charge-transfer fluorescence, for example, the formation of exciplexes in anthracene/dimethylaniline [77], 1-cyanonaphthalene/triethylamine [78], tetracyanoethylene/4-xylene [79] and anthracene/ammonia [79]. It is interesting to note that the 1-cyanonaphthalene/triethylamine produces features blue-shifted from the origin. A general indication that a charge transfer type interaction has taken place being the observation of broad red-shifted fluorescence [74].

Excited-state intramolecular proton transfer (ESIPT) has been observed in the supersonic jet 1) 2,5-Bis(2-benzoxazilyl)hydroquinone, A, [80,81] and 2) 2,5-Bis(2-benzothiazoly)hydroquinone, B, [82], the requirement being the possession of the an intramolecular

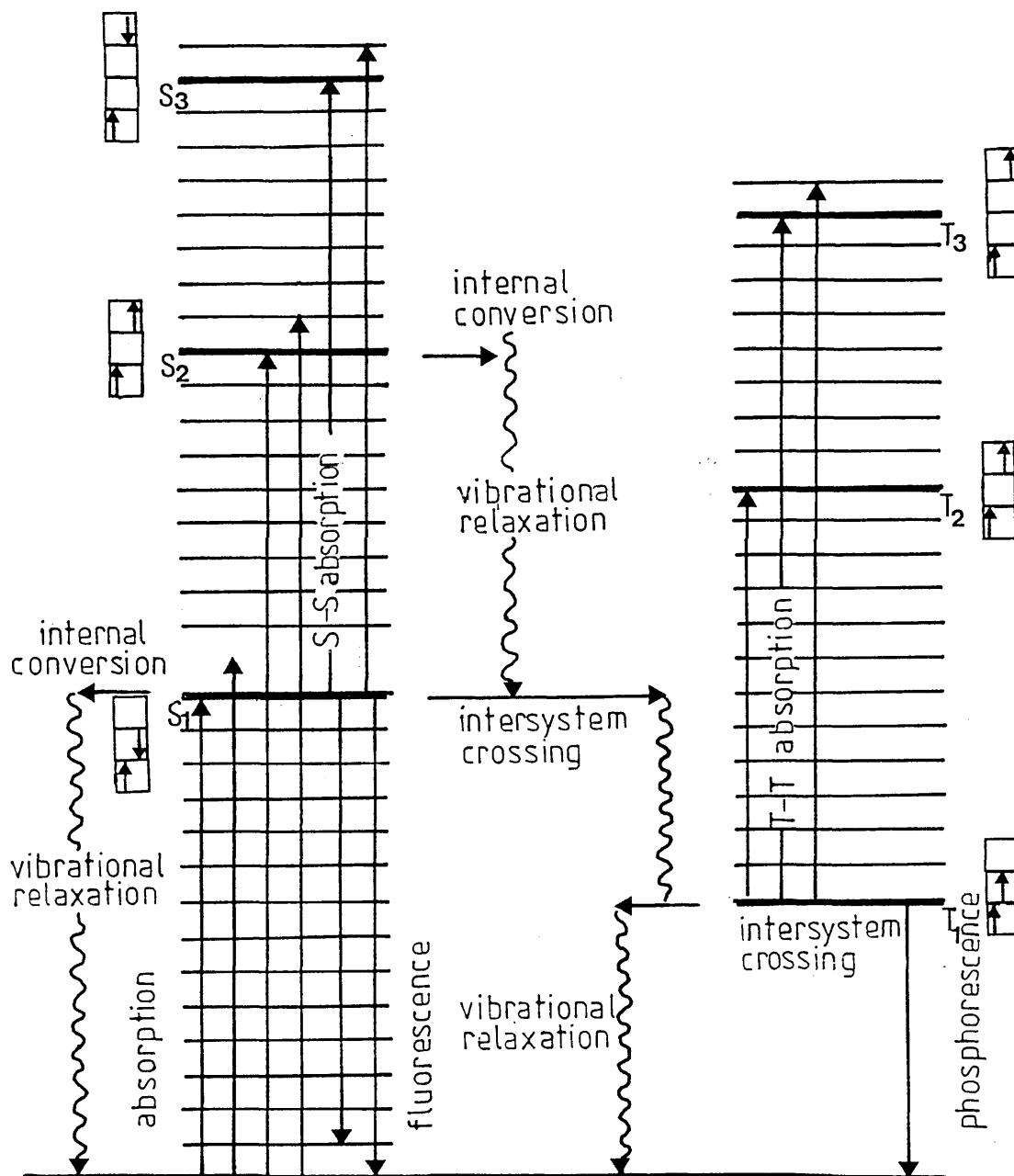
hydrogen bond (tautomerism) between a phenolic hydroxyl group and some nearby heteroatom of the same chromophore, ESIPT being characterised by a broad red-shifted ($\sim 7000\text{ cm}^{-1}$) anomalous fluorescence. This effect is often complicated by specific hydrogen bonding or by the existence of distinct conformers having different internal sites in solution. Dual fluorescence was observed in the supersonic jet for A, with only red fluorescence for B, suggesting that there was no significant intrinsic barrier to ESIPT.

A compound thought to undergo TICT formation, 9,9'-bianthryl, has been studied in the supersonic jet [63] where it was found that charge transfer occurs on the addition of one acetone molecule to the solute [64]. However, in this case, no evidence is given for the 1:1 stoichiometry, and it is not ruled out that higher complexes were responsible for the charge-transfer fluorescence. Hence, a* fluorescence from DMABN could be expected to be observed under super cooled conditions.

1.5 NON-RADIATIVE DECAY

The modified Jablonski diagram (figure 1.10) illustrates the various mechanisms of non-radiative decay. These mechanisms have been discussed and reviewed in many publications in the solution and gas phase [9,83] and in the cold-isolated state [84]. Of particular interest is non-radiative decay via intramolecular

Figure 1.10 Jablonski diagram illustrating the processes connecting the various electronic states.



vibrational redistribution studied in the supersonic jet.

1.5.1 Intramolecular vibrational redistribution

Intramolecular vibrational redistribution (IVR) is one of the most rapid deactivation processes, occurring on a picosecond timescale. The process involves the temporal evolution of a vibrationally excited state, populated by optical or other means into a set of vibrational states but involving no change in electronic state. The advent of the microchannel plate (having the advantage of a FWHM of approximately 10 ps) and combination with a supersonic jet enables the study of single vibronic level absorption in aromatic molecules and their subsequent evolution without collisional perturbation [84-88].

Many different aspects of chemical behaviour involve reorganisation of internal energy by intramolecular vibrational redistribution (IVR) [87]. The basic point underlying IVR is that excitation sources having finite spectral width corresponding to pulsed fields are unable to excite single eigenstates of the excited state potential surface once these states become too congested. This arises because at some point of inspection all these exact eigenstates can undergo radiative transitions. Thus the congested regions may be probed by using better spectral resolution or by more careful studies of the decay patterns (complex quantum beats). At some excess energy a situation will arise

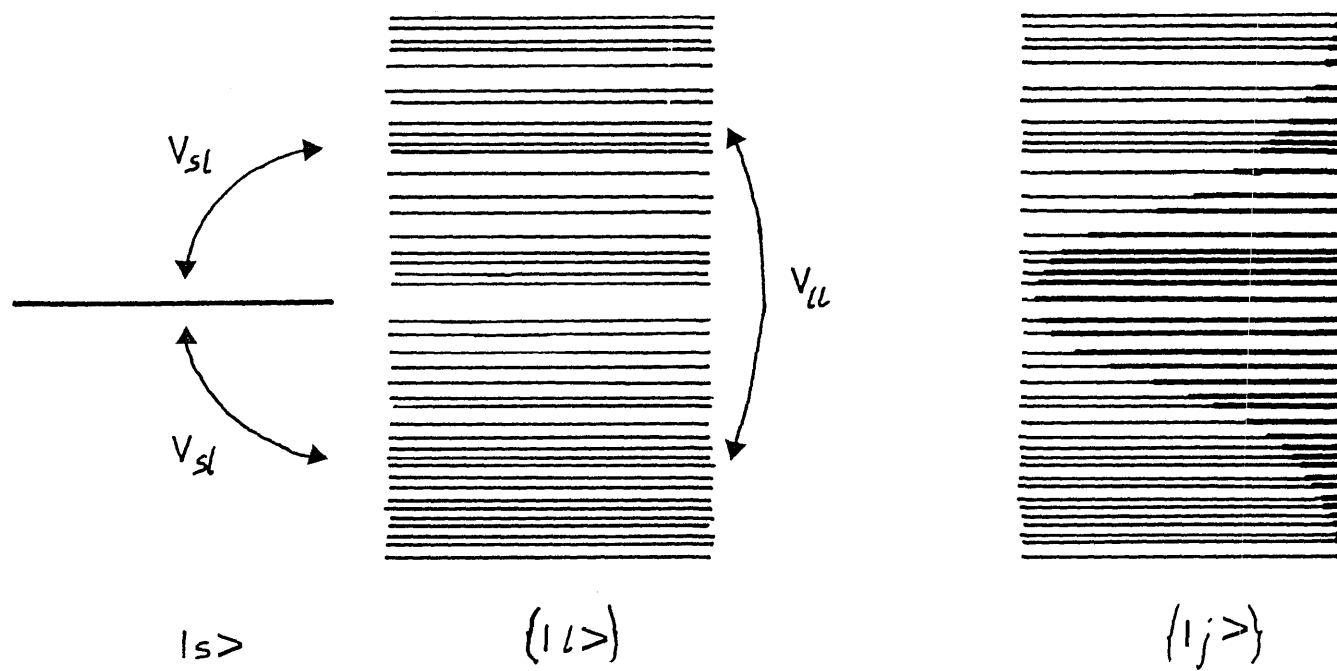
where spectroscopic analysis does not yield information regarding the respective eigenstates of the upper surface. This is the onset of the so called statistical limit. The coupled levels can still be explored experimentally in as much as their populations change in time no matter what type of light source is used to probe the spectrum.

The ability to excite a variety of known initial S_1 vibrational distributions in a given molecule allows the systematic study of IVR as functions of excess vibrational energy and initial vibrational identity. The onset of IVR, known as the threshold, are low in a variety of aromatics and heteroaromatics occurring within the first few thousand cm^{-1} of excess vibrational energy. The vibrational level densities vary in range from a few states (or less) per cm^{-1} to hundreds of states per cm^{-1} [85].

The collision-free fluorescence experiment is understood within the context of the level-mixing model shown in figure 1.11. On considering a field of zero-order states (for example, harmonic), not necessarily overlapping by their widths, that are mixed with average coupling matrix elements $V_{11} \sim V_{s1}$. The $|s\rangle$ level has a larger oscillator strength (on account of a favourable Frank-Condon factor) to a thermally populated level in the ground electronic state whereas the $\{|1\rangle\}$ levels do

Figure 1.11 Schematic of mixing of zero-order vibrational levels within a singlet electronic state.

53



not. In the absence of coupling, the $|s\rangle$ level would give rise to a bright and discrete feature in the $S_1 \leftarrow S_0$ absorption spectrum even though that level is surrounded by a thick field of S_1 levels. In reality, the coupling disperses the $|s\rangle$ character in a quasi-Lorentzian distribution over the field so that the absorption now has the structure of the dispersion. If the level structure is sufficiently sparse, the dispersed multi-line structure can be directly observed, but this has been a rare situation for cases other than a few Fermi-level resonances [85]. More commonly the coupling is so small relative to the experimental resolution (often limited by thermal inhomogeneous broadening) that the $|s\rangle$ state dispersion is not readily detected. In these cases the absorption may still appear "sharp" under conditions of moderate spectral resolution.

The fluorescence spectrum, however is extremely sensitive to such mixing. It can reveal mixing that is quite undetectable in absorption. The excitation bandwidths span much or all of the coupling width, and the ensuing fluorescence is a superposition of so many single vibronic level spectra that the fluorescence congestion becomes a quasi-continuum. By this means, "sharp" absorption can yield unstructured collision-free fluorescence.

The threshold measurements generally rely on the appearance of unstructured emission as the indicator

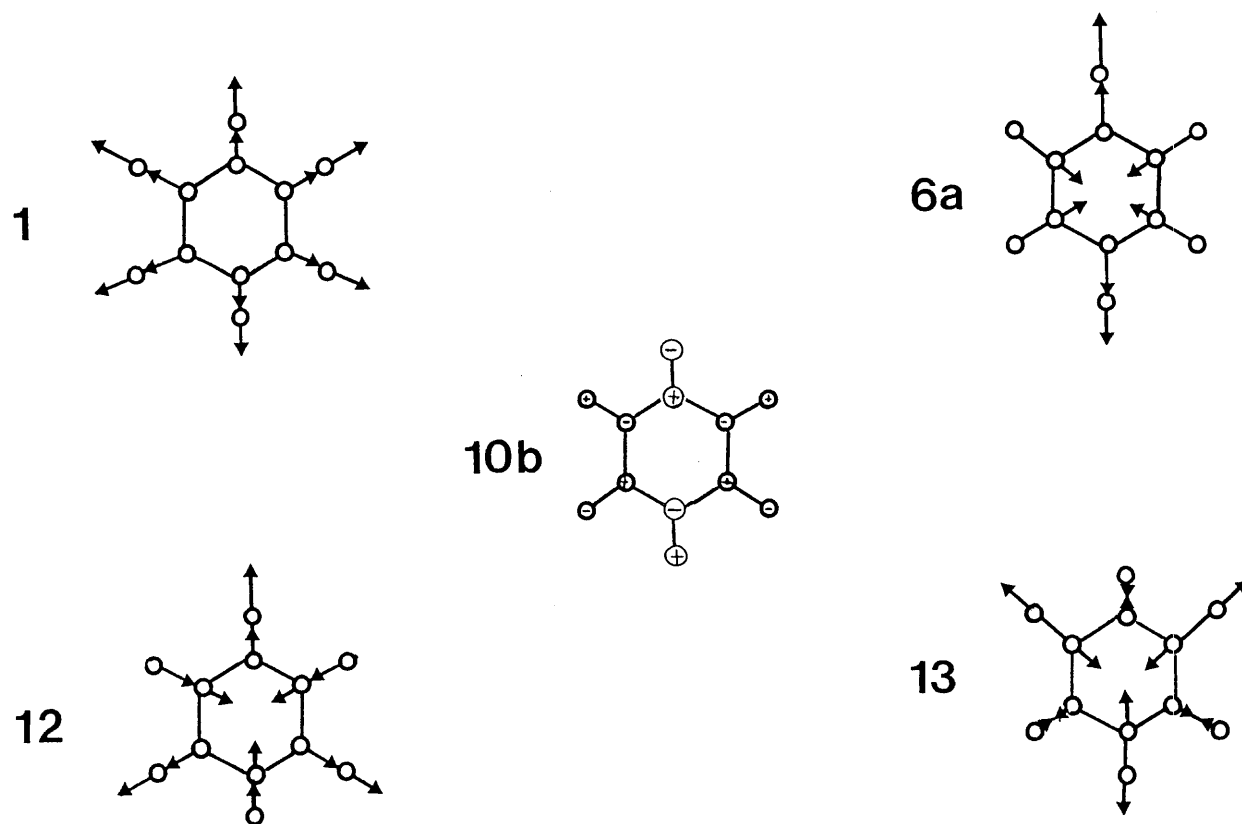
of IVR when an excitation laser is tuned to successively higher S_1 regions. Fluorescence congestion is a sensitive marker and the appearance of congestion beyond that expected from thermal inhomogeneous broadening is a sure indication of the extensive level mixing that is a necessary prerequisite of IVR.

1.6 VIBRATIONAL MODES OF BENZENE

The normal modes of vibration referred to in this thesis are those that are applied to benzene. This is a formal treatment since the normal vibration of a benzene derivative cannot be related to any normal mode of benzene by a continuous function because the substitution introduces qualitative changes into the properties of the mechanical system represented by the molecule. However, the benzene nucleus dominates in the determination of the force field of the vibrating molecule, so that following the principles of symmetry perturbation procedures the normal modes of a derivative can be compared to the appropriate normal vibration of benzene [89].

There are twenty normal vibrations of benzene. The work here is only concerned with several of these: 1, 6a, 10b, 12 and 13. These are shown in figure 1.12 together with table 1.1 which gives the frequency regions for the selected fundamental vibrations of relevant benzene derivatives [89]. The substituents considered

Figure 1.12 Selected fundamental vibrations of benzene.



here are all classed as "light", that is, the first atom of the substituent has an atomic weight of less than 25.

Vibrational mode 1 is the symmetric ring breathing mode of benzene and is a substituent sensitive vibration. Vibrational mode 6a involves C-C-C in plane bending of the benzene ring. Vibrational mode 10b corresponds to C-H out of plane bending of the benzene ring. Vibrational mode 12 involves C-C-C trigonal bending of the benzene ring. Vibrational mode 13 involves C-H stretching of the benzene ring carbons.

Table 1.1 Frequency regions for selected normal vibrations of benzene derivatives.

	monolight cm ⁻¹	1,2-dilight cm ⁻¹	1,3-dilight cm ⁻¹	1,4-dilight cm ⁻¹
1	620-830	630-780	650-750	720-860
6a	300-530	530-600	450-550	330-510
10b	880-910	820-870	840-880	890-940 (240-300) (diheavy)
12	990-1010	750-860	990-1010	680-760
13	1100-1280	1080-1270	1120-1300	1100-1320

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CHAPTER 2

EXPERIMENTAL

2.1 THE SUPERSONIC JET

A supersonic jet allows the preparation of internally cold, isolated, gas phase molecules.

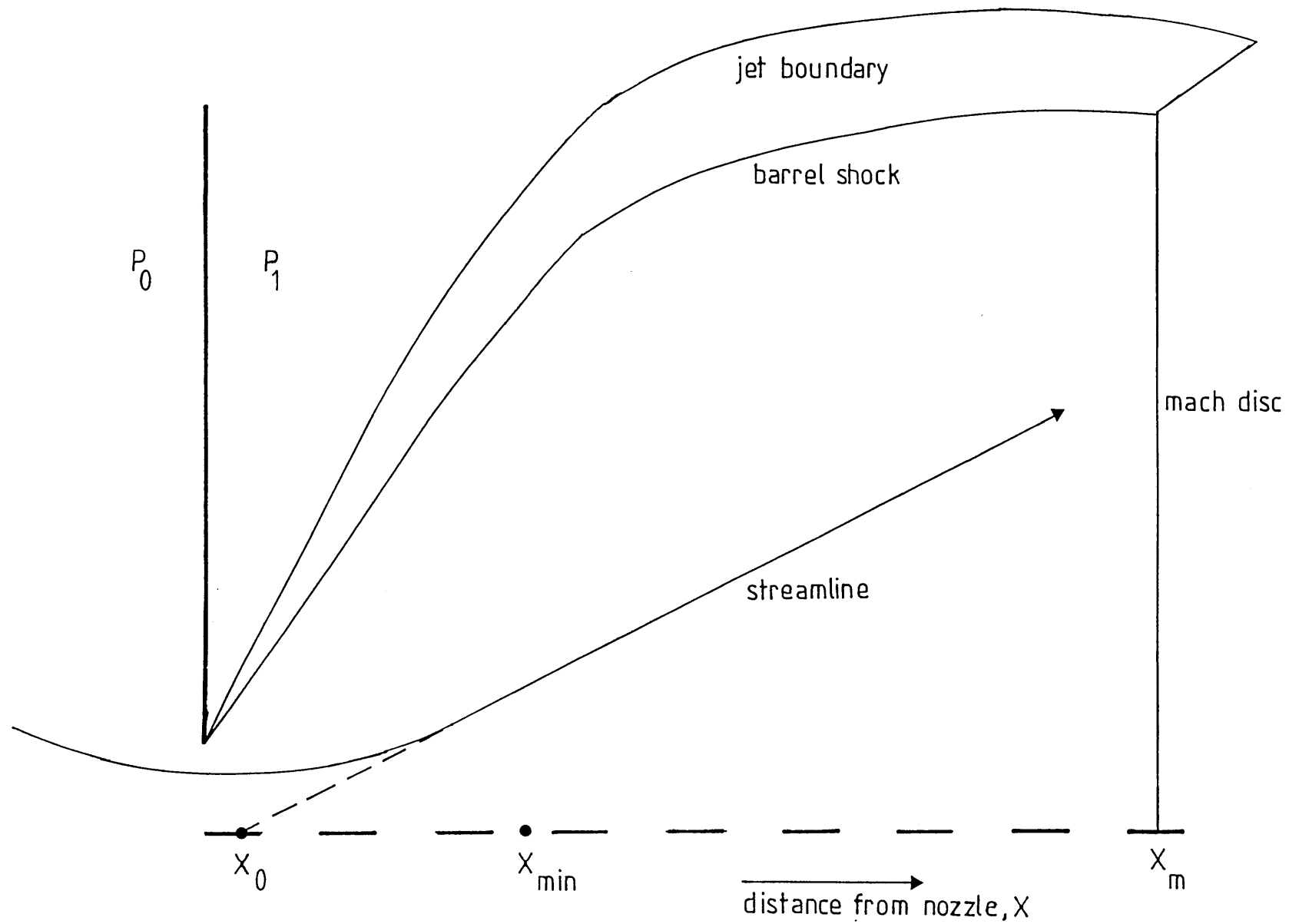
The use of supersonic expansion was initially explored by Kantrowitz and Grey [1]. The spectroscopic implications of supersonic expansion were later recognised by Huber and Douglas [2] who proposed that a supersonic free expansion of a polyatomic gas would lead to the simplification of absorption spectra of notoriously complicated molecules such as NO_2 and NO . The advent of laser technology provided a useful stimulus to the development of supersonic expansions. The technique was further advanced by Sinh et al [3] for their study of alkali dimers and by Smalley et al for their investigation of NO_2 [4,5].

2.1.1 Supersonic jet, theory

A supersonic free jet is produced when a reservoir of gas at relatively high pressure, P_0 , is allowed to discharge through a small orifice of diameter, D , into a lower background pressure of P_1 . The small orifice may be in the form of a circular hole in a thin wall (as in this experiment) or as a rapidly converging axisymmetric nozzle. Initially, the molecules in the jet, downstream of the nozzle, undergo many binary collisions in which the translational velocity

distribution, along the axis of the jet, is narrowed by an order of magnitude [6]. The narrowing of the velocity distribution represents an apparent reduction in the translational energy of the molecules. In order to maintain equilibrium between all the degrees of freedom of the molecule, the vibrational and rotational degrees lose energy to the translational degrees of freedom, hence, cooling of the vibrational and rotational states is achieved. As the expansion proceeds the density of the gas drops and eventually becomes too low to provide the collisions necessary to connect the internal degrees of freedom with the translational bath. In the absence of collisions, no energy can flow from the internal degrees of freedom. The state that the system had when it entered the collision free region is frozen from then on downstream. Those degrees of freedom that equilibrate most rapidly with the translational bath are coldest at the point where the expansion runs out of collisions. Due to condensation being a much slower process than rotational or even vibrational relaxation, extensive internal cooling can be achieved before condensation takes place. It is this region of the supersonic jet that provides the required area of study. Figure 2.1 shows a computed free jet flow [7]. Initially there is cylindrical flow followed by a flow as if from a point source. Inside the barrel shock the streamline appears to radiate from a source at a distance X_0 , downstream of the orifice where the density is sufficiently low so that

Figure 2.1 Schematic diagram of a free jet flow.



there are no collisions and the Mach number and temperature is frozen from this point on downstream until interactions with background gas become important. The Mach disc is a shock boundary and marks the transition from free molecular flow, where the gas is unaware of the chamber, to thermal motion which approaches the chamber temperature [8], hence providing a source of heating and limiting the cooling effect of the expansion.

2.1.2 Variation of temperature with distance from nozzle

Under ideal conditions, that is, without viscous forces; heat conductivity; shock waves due to collisions with background gas; heat sinks such as chemical reactions and the absence of heat conductivity, the expansion will be isentropic. For a perfect gas the temperature, pressure, density and Mach number profiles are controlled by thermodynamics and are related by the equation [9]:

$$\begin{aligned} \left(\frac{T}{T_0}\right) &= \left(\frac{P}{P_0}\right)^{(\gamma-1/\gamma)} \\ &= \left(\frac{\rho}{\rho_0}\right)^{(\gamma-1)} \\ &= \left(\frac{1+(\gamma-1)}{2M^2}\right)^{-1} \end{aligned} \quad (1)$$

ρ_0 = density of reservoir

T_0 = temperature of reservoir

P_0 = pressure of reservoir

T = temperature of expansion

P = pressure of expansion

ρ = density of expansion

$\gamma = C_p/C_v$ = heat capacity ratio

M = Mach number = ratio of flow velocity, v , to the local speed of sound. (This is greater than 1 not because of large particle speeds but because the local speed of sound is given by $(\gamma RT/m)^{1/2}$ and is small under these conditions.)

For a continuous gas at distances greater than a few nozzle diameters from the orifice it has been shown [8] that the Mach number is given by:

$$M = A \left(\frac{X}{D} \right)^{(\gamma-1)} \quad (2)$$

X = distance downstream

D = nozzle diameter

A = a constant dependent on γ and is = 3.26 for a monatomic gas

The above equation, (2), only describes the Mach number development in the region where the density is high enough to provide the two body collisions required for cooling. For the region where there are no collisions Anderson and Fenn [6] have predicted that for a monatomic gas, the terminal Mach number, M_T , is a function only of the product $P_0 D$ and, for argon, is given by:

$$M_T = 133(P_0 D)^{0.4} \quad (3)$$

P_0 = reservoir pressure in atmosphere

D = nozzle diameter in cm

In the case of He, the quantum effects cause the collisional cross section to increase with decreasing relative energy leading to greater terminal Mach numbers than those predicted by (3). For this experiment, using $P_0 = 0.08$ and $D = 0.02$ gave $M_T = 10.1$ corresponding to a translational temperature, $T_T = 10.6K$ and a value of $X = 1.4mm$ obtained from equations (1) and (3) for argon.

The useful region for spectroscopic investigation can be found from:

$$X_m = 0.67D \left(\frac{P_0}{P_1} \right)^{1/2} \quad (4)$$

where X_m is defined by figure 2.1

for which He, H_2 and D_2 do not conform despite being independent of δ .

For argon, and in our case, using results obtained from (1) and (3) where the background pressure was less than 0.06 Torr and actually nearer 1×10^{-3} Torr, a value of $X_m > 4.2mm$ was obtained. On the basis of calculations used so far, the useful region for spectroscopic investigation lies between $1.4mm < X < 4.2mm$.

Adding a small quantity of polyatomic molecules is thought to have a negligible effect on cooling because

of the large number of collisions undertaken before M_T is reached.

2.1.3 Sample density variation with distance from nozzle

An isentropic expansion requires that the density of a gas falls proportionally with X^2 (where X is the distance from the nozzle) as shown in figure 2.1 where X_0 is the axial virtual origin and $X_{\min} = 2.5D$ for argon.

The sample density variation is given by:

$$\frac{\rho}{\rho_0} = \left(\frac{X_T}{X}\right)^2 \cdot \left(\frac{T_T}{T_0}\right)^{(1/\gamma-1)} \quad (5)$$

for $X_{\min} < X < X_0$

X_T is found from M_T given by equations (2) and (3) T_T can be found from M_T and equation (1). By using argon as the carrier gas and putting $X = 4\text{mm}$ the ratio ρ/ρ_0 is approximately 8.2×10^{-4} . The sample vapour pressure is approximately 1mB. Hence, assuming the perfect gas law the sample density at 4mm is 2.14×10^{16} per litre (equivalent to 3.55×10^{-8} Molar).

2.1.4. Residence time in excitation beam

The length of time the sample will be exposed to the excitation source will be dependent on the velocity of the said molecules and the geometry of the excitation optics. The maximum mean translational

velocity for helium, argon and nitrogen is found from [10]:

$$v_{\infty} = \left(\frac{\gamma}{\gamma-1} \right)^{1/2} \left(\frac{2k_B T_0}{M} \right)^{1/2} \quad (6)$$

giving values of 2012, 636 and 901ms⁻¹ respectively at 373K. Unless the terminal Mach number has been reached the velocity at the point of investigation will be a fraction of this. The speed of the sample molecules can be found from [10]:

$$\frac{v}{v_{\infty}} = M \left(\frac{(\gamma-1)T}{2T_0} \right)^{1/2} \quad (7)$$

assuming the velocity slip for argon is negligible. For helium at 4mm the terminal Mach number has not been reached. Values of $M = 24.2$ and $T = 1.9K$ are obtained from equations (1) and (2) giving a value for v of 1990ms⁻¹, though this velocity may not be accurate because the sample molecules are known to have a large velocity slip depending on pressures used [11].

The diameter of the excitation beam was 0.5mm for the excimer pumped dye laser and 0.1-0.2mm when using the argon pumped dye laser. Using the above estimated value of v for helium, the residence time corresponds to 0.25μs and 0.08μs respectively. In the case of the argon ion pumped dye laser, where the laser is pulsed at 4MHz, if the arrival of a sample in the

excitation region coincides with a laser pulse of duration of 10ps it will experience just one more pulse before leaving this region. In the case of the excimer pumped dye laser, which is pulsed at 10Hz, only one pulse is experienced on the molecule arriving in the excitation region.

The measurements of lifetimes are limited to the residence time. If the molecules remain excited at distances greater than 4mm from the excitation region then they are not detected due to being outside the range of the collection optics.

2.1.5 Formation of van der Waals complexes

An important feature of the seeded supersonic jet is the formation of van der Waals complexes. Due to the very low temperatures obtained in the free jet, the very small binding energies of complexes formed between the seed molecule and the carrier gas exceed the internal energy of the molecules from which they are formed. Their presence, in general, is not desirable due to producing red-shifted features in the excitation spectrum. In argon these complexes are readily formed with a backing pressure of greater than one atmosphere. In helium these complexes are less readily formed. By restricting the backing pressure the complex formation with the carrier gas could be suppressed. It will be apparent from Chapter 1 that formation of van der

Waals complexes forms an important part of this research.

2.1.6 Vibrational and rotational temperature

Laser spectroscopy of large molecules cooled in supersonic expansions [9,11,12] reveals well-resolved spectral features for the electronic origin and vibrational excitation of the lowest spin allowed electronic transitions. The line widths (full width half maximum) of individual electronic vibrational excitations of large molecules such as benzene [13] and its derivatives [14], naphthalene [15], anthracene [16], phthalocyanine [17] and porphyrins [18] in seeded supersonic expansions of He or Ar are typically $1\text{-}3\text{cm}^{-1}$ with the line width essentially originating from rotational broadening.

Quantitative information on cooling was required rather than the observation that effective vibrational and rotational cooling resulted in ultracold molecules. Methods have been advanced to determine temperatures. Translational temperatures, T_T , of both diatomic [19] and large molecules [20] can be inferred from thermodynamic hydrodynamic relations for the diluent [2] though they are subject to some limitations due to velocity slip [20]. Vibrational temperatures, T_v , can be surmised from hot band spectroscopy and have been determined for both diatomic and large molecules [20]. Determination of rotational temperature has also been

carried out for diatomic [19] and large molecules [21] using rotational constants of the ground and excited states.

From measurements carried out with carbazole, in the jet apparatus described in this thesis, a vibrational temperature of approximately 50K was determined and a rotational temperature of less than 10K.

2.1.6 Supersonic Jet, experimental

The apparatus is depicted in figure 2.2, the dominant feature being the vapour booster pump (Edwards 18B4A) which provides a throughput capacity of 4000ls^{-1} at 10^{-4} to 10^{-1}mbar via heating silicone oil (Edwards booster grade 200) to 180°C . The booster pump is backed by a large rotary pump (Edwards EM 275) capable of a throughput of 100ls^{-1} at 1mBar pressure which is the typical input pressure of the booster pump. To allow access to the chamber during an experiment, without letting the pumps up to air, a large baffle valve was incorporated into the expansion chamber, operated by compressed nitrogen. The oven-nozzle assembly is shown in figure 2.3a and is supported by the top flange of the expansion chamber. The sample is placed in a stainless steel tube and is heated by resistive heater elements. Heating is limited by the presence of PTFE foam backed tape (180°C) which is used to provide the oven seal.

The nozzles are made from $1/4"$ OD stainless

Figure 2.2 Diagram of the supersonic jet apparatus.

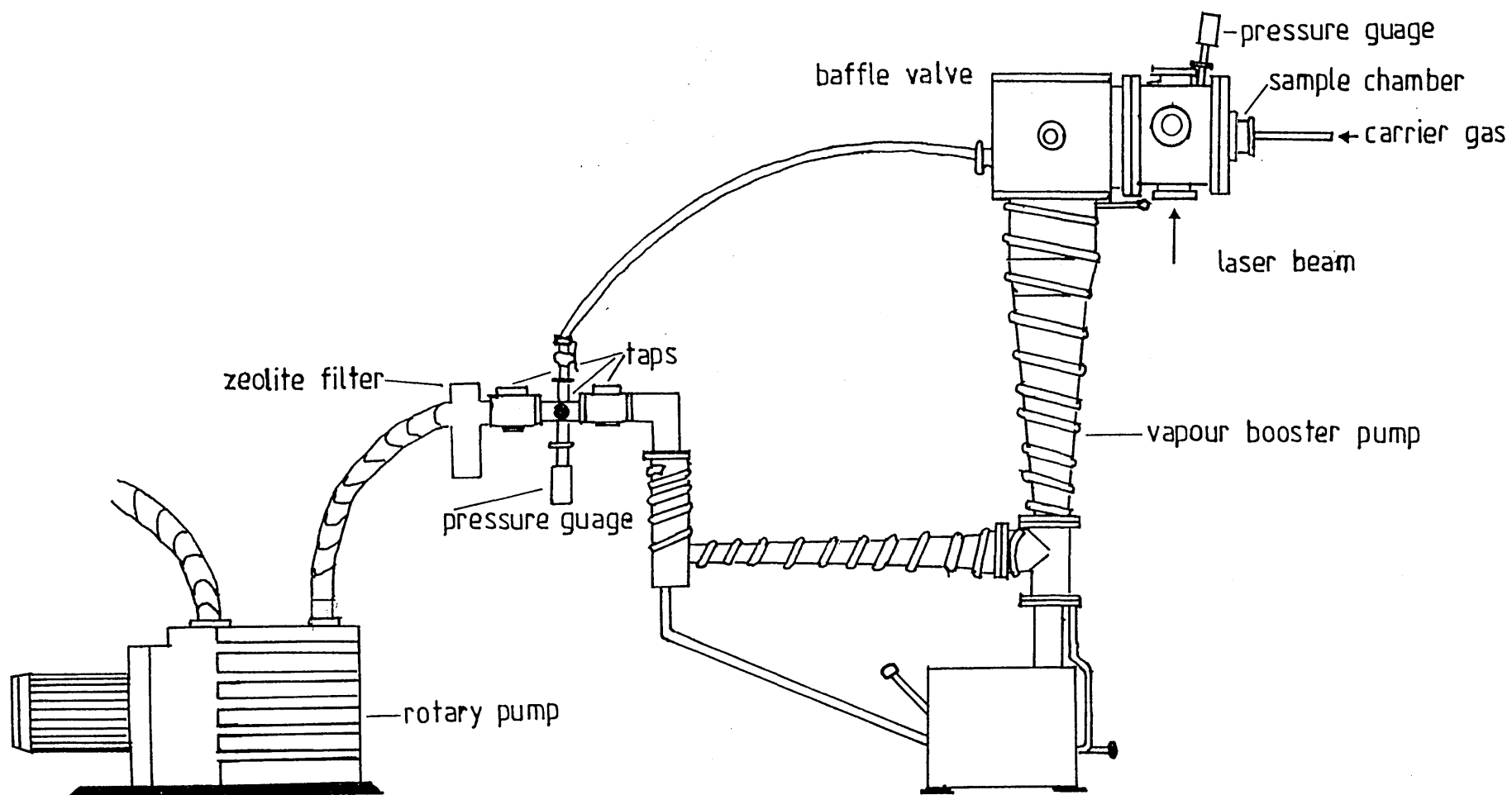
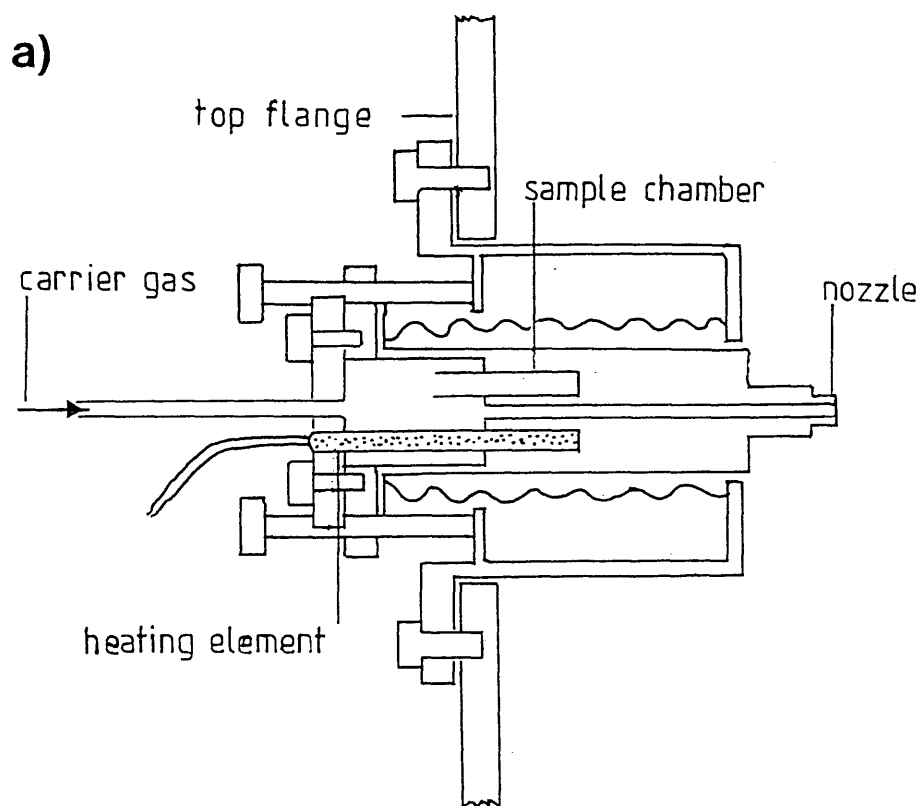
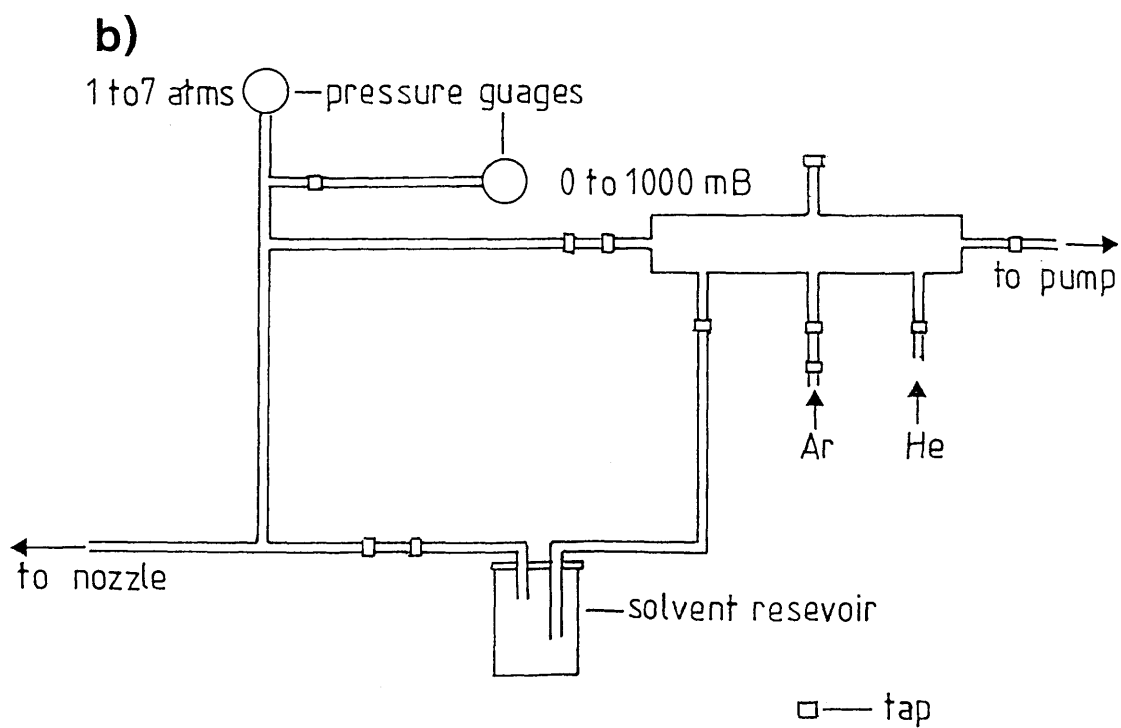


Figure 2.3 a) Oven nozzle assembly.



b) Gas handling line.



steel or "Dural" cylinders, internal diameter of 1/8" and drilled through the end wall, 0.005" thick by Drill services Ltd (Horley). The orifices range from 50 to 500µm in diameter.

A zeolite trap (figure 2.2) is used to prevent organic molecules escaping to the atmosphere, though the majority of substance was deposited on the inside walls of the chamber. This was cleaned at regular intervals and then covered with matt black paint to prevent internal reflections.

Figure 2.3b shows the gas handling line built to introduce regulated quantities of solvent into the expansion. Solvents were placed in the reservoir and the flow controlled by the fine taps. The mole fraction was expressed as:

$$MF = \frac{V_p}{P_m (1 + a/b)} \quad (8)$$

V_p = solvent vapour pressure at a given temperature

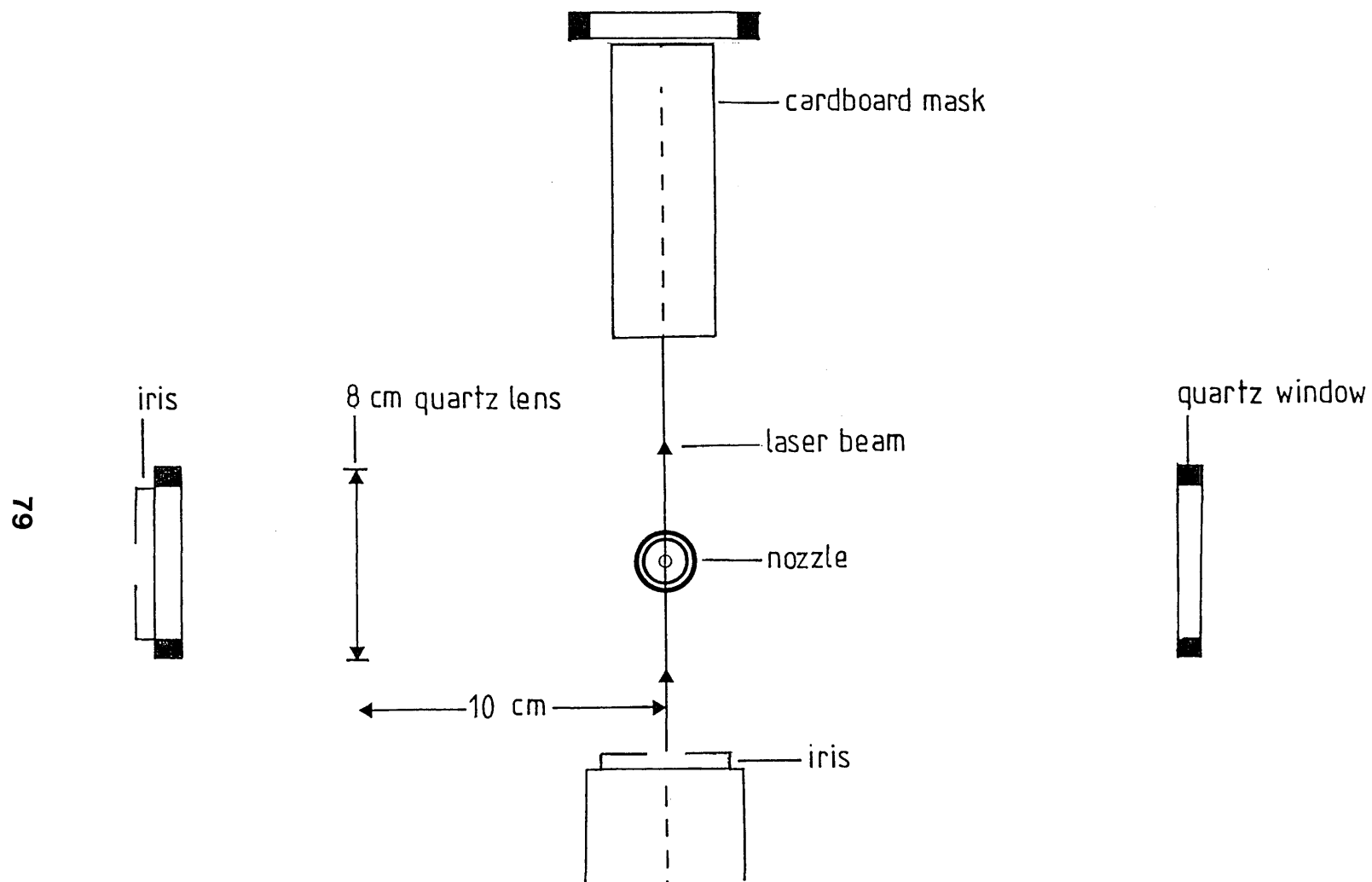
P_m = carrier gas pressure in the manifold

a = flow rate through tube a

b = flow rate through tube b

Scattered laser light from the surface of the top quartz window was negated by the use of a beam stop (figure 2.4).

Figure 2.4 Diagram of the expansion region.

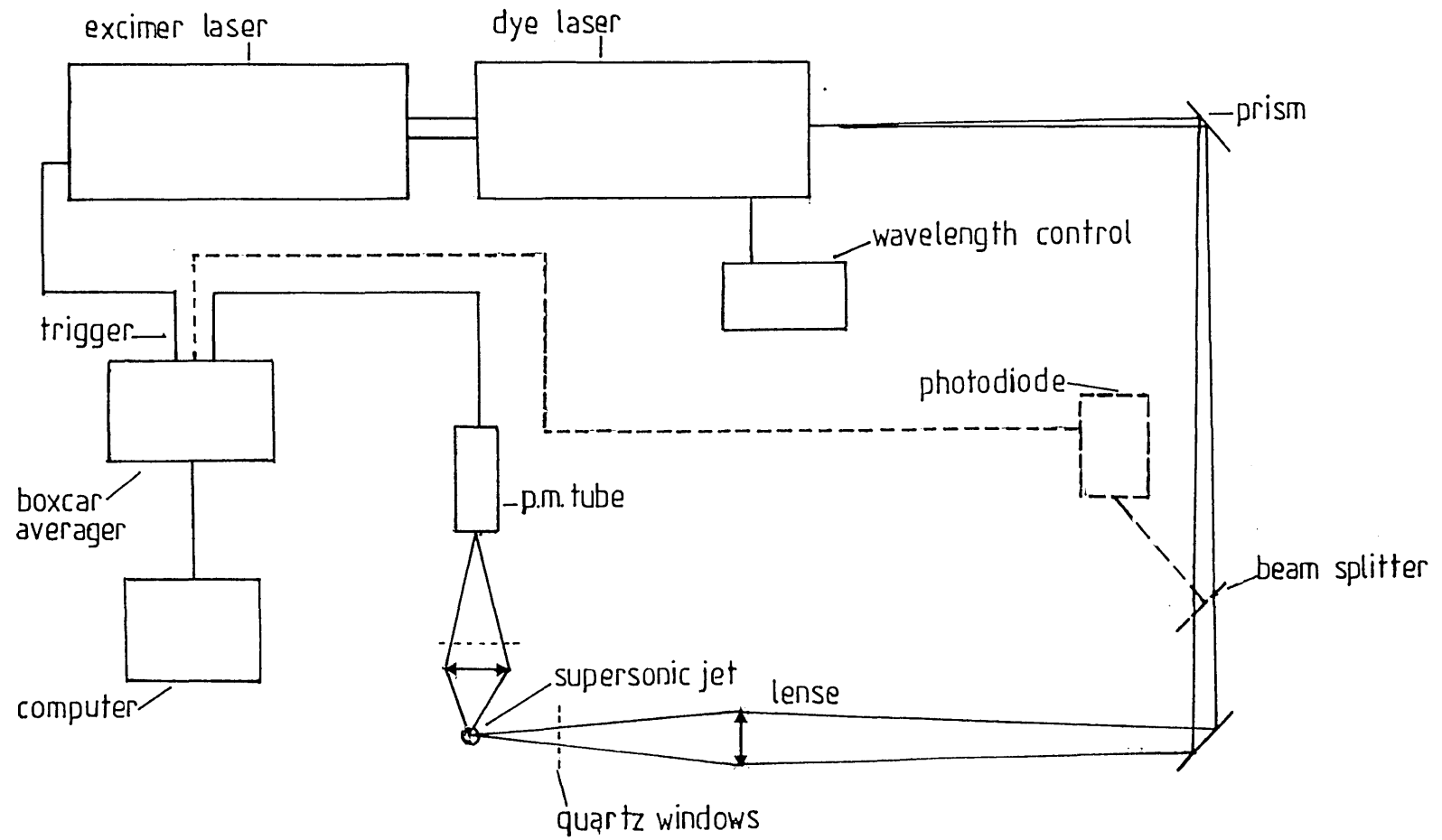


2.2 THE MEASUREMENT OF FLUORESCENCE EXCITATION SPECTRA

2.2.1 Method

A diagram of the apparatus used to measure the fluorescence excitation spectra of the molecules of interest is shown in figure 2.5. The excitation source was a frequency tunable excimer-pumped dye laser with the output frequency doubled (LAMBDA PHYSIK MSC, 103/FL2002). The laser beam was directed into the expansion chamber via the quartz prisms. The beam was then focused into the path of the supersonic jet expansion, 4mm away from the nozzle, by a quartz lens. This was carried out before the experiment was run with the baffle valve closed. Correct alignment of the photomultiplier tube (PM tube) and collection lens was checked by placing a quartz scatterer in front of the beam and ascertaining that on closing down of an iris in front of the collection window (figure 2.4), the laser beam traversed the centre and was focused into the PM tube. On detection of the fluorescence, the output from the PM tube was fed into the boxcar averager (see section 2.2.4). Because the intensity of the laser beam varies when tuning the dye laser, a part of the laser beam was split off using a 0.04 OD neutral density filter and aligned into a photodiode or PM tube. The output from this was fed into a second boxcar averaging unit. The trigger for the boxcar was obtained from the synchronous

Figure 2.5 Diagram of the apparatus used to measure fluorescence excitation spectra.



output of the excimer laser power supply. The resulting spectrum was recorded with a chart recorder or on a computer.

2.2.2 The Excitation source

The experimental set up underwent a recent major update when the original excitation source, a xenon arc lamp was replaced with an excimer pumped dye laser system. Although this was a commercial system, the mode of operation is complex and a full description will be given here.

2.2.2a The Excimer laser

Excimer lasers are pulsed gas lasers that use a mixture of a rare gas and a halogen as the active medium. The concept of using a bound-free excimer system as a lasing medium was originally proposed in 1960 [22]. However, it was not until 1972 that the first successful laboratory demonstrations were made. It was the application of electron beams which enabled a sufficiently high excitation rate to achieve the optical amplification required. The first rare gas halogen excimers were discovered in 1975 [23,24] and are presently one of the most highly developed excimer systems.

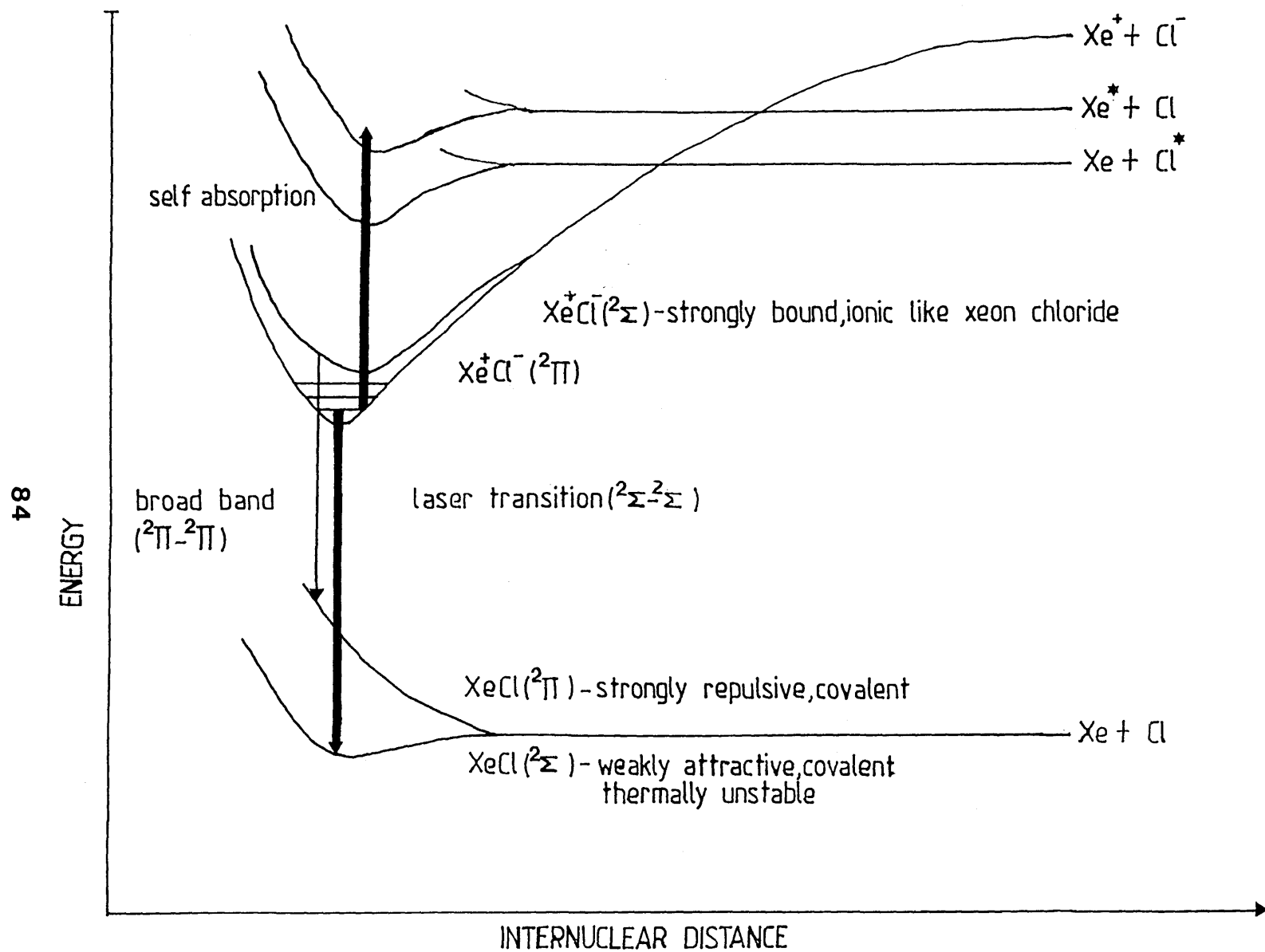
Theory

The interaction of the ground states of two

closed-shell systems (atom or molecule) is usually repulsive except for a weak long-range van der Waals interaction or electrostatic interaction. Nevertheless, interaction of an excited state with the ground state of the same fragment can form a strong chemical bond. The bound excited state is known as an excimer (for like atoms/molecules, see section 1.3.1) or exciplex (for unlike atoms/molecules see section 1.3.4). The bound to continuum transition defines an excimer emission system [25]. The xenon chloride rare gas halide system, as it is the excitation source used in this experiment, will be discussed in depth in order to illustrate the excimer system.

The potential energy diagram (figure 2.6) gives the general structure of the Xe and Cl atoms. The ground state is covalently bonded and corresponds to the ^1S Xe and the ^2P Cl atoms at infinite internuclear separation. The ground state manifold consists of two states because of the P character of the Cl atom. Of these, the $^2\Sigma$ has the lowest energy since in this configuration the singly occupied Cl orbital is directed toward the Xe atom. This forms the ground state and is referred to as the X state. It is weakly bound (255cm^{-1}) in XeCl [26]. The upper laser level is an ionically bound charge-transfer state correlating to the ^2P Xe positive ion and the ^1S chlorine negative ion at infinite internuclear separation. The potential of this state

Figure 2.6 Potential energy diagram for the XeCl excimer.



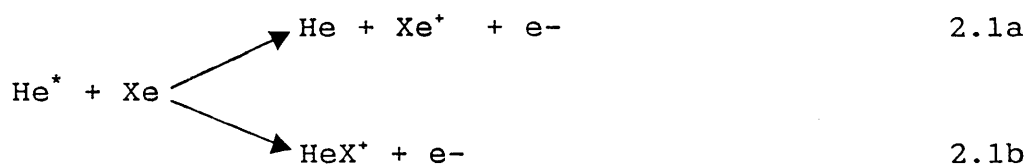
follows a coulomb curve in an adiabatic sense, the covalent curve correlating to the excited state potential of the Xe and Cl atoms. The structure of the ionic upper level manifold is similar to that of the ground state manifold with the $^2\Sigma$ state lying lowest. This is referred to, by convention, as the B state. The emission spectrum of XeCl consists of several bands as shown in figure 2.6. The strongest band is assigned to the $B(^2\Sigma) \rightarrow Cl(^2\Sigma)$ transition and gives rise to the laser transition observed in XeCl (308nm).

Reaction Kinetics

The reaction kinetics of rare gas halide lasers are complex involving several ground state atomic and molecular species, several ionic species and a large number of excited atomic and molecular species. Although the kinetics of the laser are not fully understood, the important aspects of laser performance can be adequately described.

In general, rare gas halide laser mixtures consist of a larger amount of a higher rare gas. In our case either Neon 70 (30% He 70% Ne) , argon or helium constitute ~93% of total gas (4% Xe and 3% HCl) were used. Electrical excitation forms excited atoms and atomic ions of the lighter rare gas species. These can dimerise, recombine with electrons and react to form diatomic and triatomic rare gas halides. Also, if the

excited species are of sufficient energy they may react with the heavier rare gas atoms as shown:



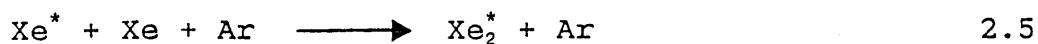
to form ions in Penning or associative ionisations reactions of the type (2.1). These reactions are generally fast and proceed at every collision. If the energy is not sufficient to produce Penning or associative ionisation then energy transfer to the heavier species may occur in reactions of the type shown below.



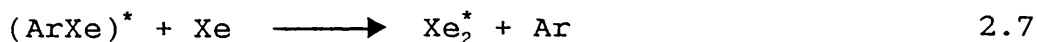
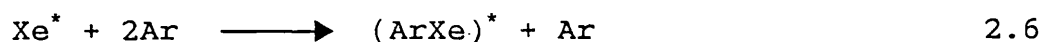
Asymmetric charge transfer between atomic ions is generally very slow at thermal energies and may be ignored. On the other hand, charge transfer from dimer ions to atoms and molecules is generally very fast.



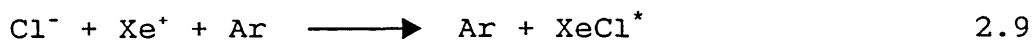
The ions and excited atoms of the heavier rare gas species can dimerise in reaction as shown in (2.5).



At low mole fractions of the rare gas, two step processes occur.



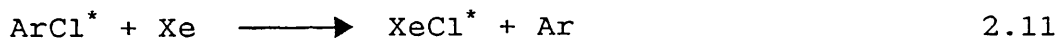
The rare gas positive ions can react with the halogen negative ions (2.8, 2.9) and the excited



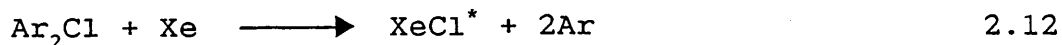
rare gas atoms and excimers can react with the halogen (2.10).



In addition, displacement reactions may occur shifting the fluorescence from the lighter rare gas halide to the heavier species as the concentration of the heavier gas is increased.



Another exchange reaction that is possible is:



The basic mechanisms by which the excited rare gas halides are formed are fast and quite efficient.

Pumping of rare gas lasers

There are two methods of pumping rare gas halide lasers, each with their own advantages.

i) Electron beam and nuclear pumped lasers

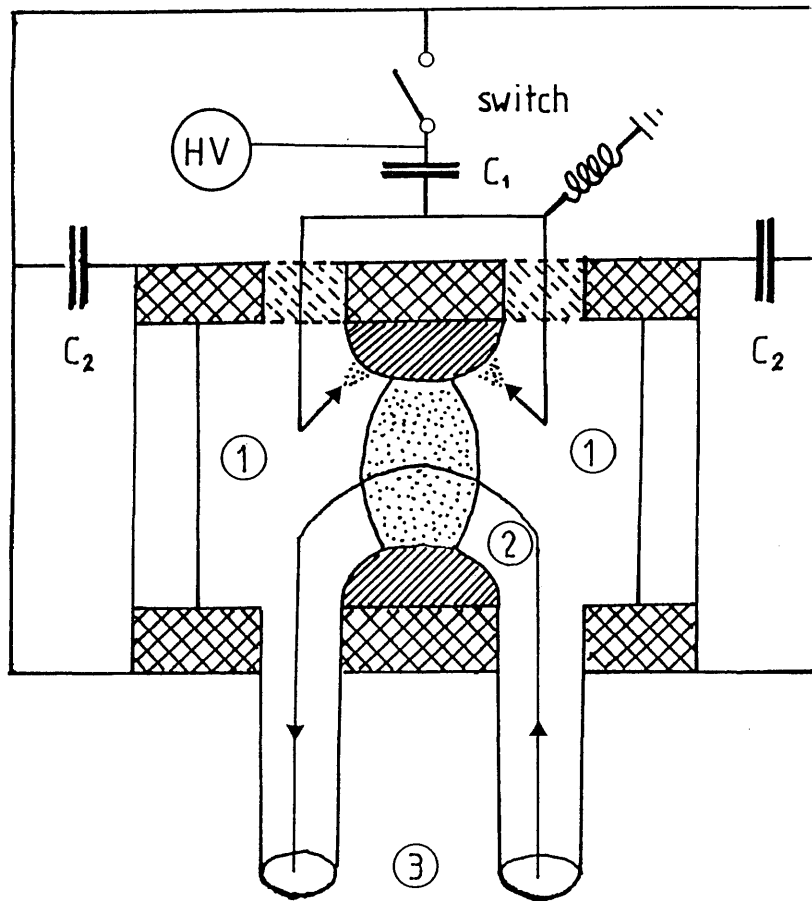
These were first used to pump rare gas halides by using high intensity relativistic electron beams [29]. Electron beams eliminate the problems of discharge stability and minimise problems of circuit inductance since they operate at higher impedances than transverse discharges.

ii) Discharge pumped lasers

Discharge pumped lasers have a higher pumping efficiency and higher average power and this is the method by which the excimer laser in this experiment was pumped. The higher pumping efficiency is achieved via a carefully controlled discharge to pump the metastable states of the rare gases directly by electron impact. Higher average power is achieved with this method.

Figure 2.7 gives a diagram of the electrical principle of the pulsed excimer laser. Losses such as by fluorescence or quenching processes, are minimised by using a fast excitation which gives rise to high output power and efficiency. A fast electrical discharge is used whose energy is first transmitted to the buffer gas.

Figure 2.7 Schematic of the electrical principle of the pulsed excimer system.



Electrical principal of the pulsed excimer laser

C_1 : main storage capacitor

C_2 : peaking capacitor

HV: high voltage power supply

switch: thyatron

1: preionization

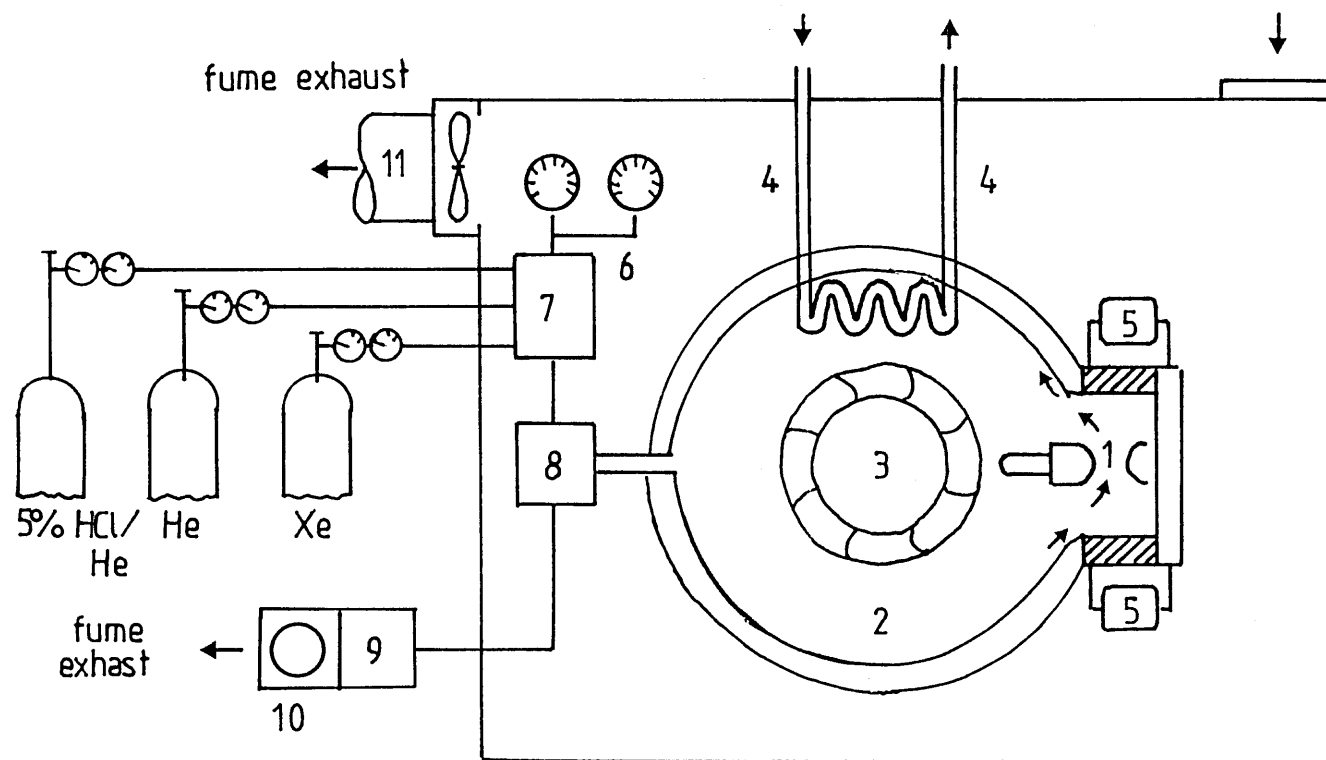
2: electrical discharge

3: gas flow

The high efficiency of these lasers is achieved by the use of well designed electrodes, efficient preionisation of the laser gas and an ultrafast, low-inductance electrical discharge circuit. The preionisation scheme produces a uniform field of ions which are free of arcs. The energy transfer from capacitor C_1 to C_2 is optimised before laser discharge, again contributing to the efficiency of output from the excimer. The thyatron is operated at low voltages (23KV in our case) giving reliable switching and low electromagnetic interference and with no misfiring.

Figure 2.8 shows the gas system. Refill of the excimer laser is an automated process. The laser is fitted with fluorocarbon insulators and metals which passivate quickly in a hydrogen-chloride environment. All electrical circuitry is outside the cavity barring the electrodes which are covered with a solid 1mm of nickel with a special compounded construction (nickel exhibits very little discharge sputtering and is reasonably resistant to chemical corrosion by HCl). The core of the electrodes is made of aluminium which has good thermal and electrical conductivity. The gas processor removes contaminated gas from the reservoir, purifies it and then redeposits the gas into the flow directly in front of the optics. This limits the cleaning of the resonator optics (a pair of flat mirrors made of calcium fluoride) to approximately once every 6

Figure 2.8 Schematic of the excimer laser gas system.



- 1 laser channel
- 2 gas resevoir
- 3 circulation fan
- 4 water cooling
- 5 capacitors
- 6 pressure meters
- 7 gas mixing
- 8 valve
- 9 filter cartridge
- 10 vacuum pump
- 11 vent outlet

months after continuous use of the fully operational laser. The lifetime of a gas fill (80mBar HCl, 100mBar Xe and 2420mBar He) is approximately 150 hours at 20Hz where the output power will drop by 40%. The laser requires water cooling of 4 l min^{-1} .

The vacuum exhaust pump is fitted with filter cartridges to remove any residual HCl and are changed every 6 months.

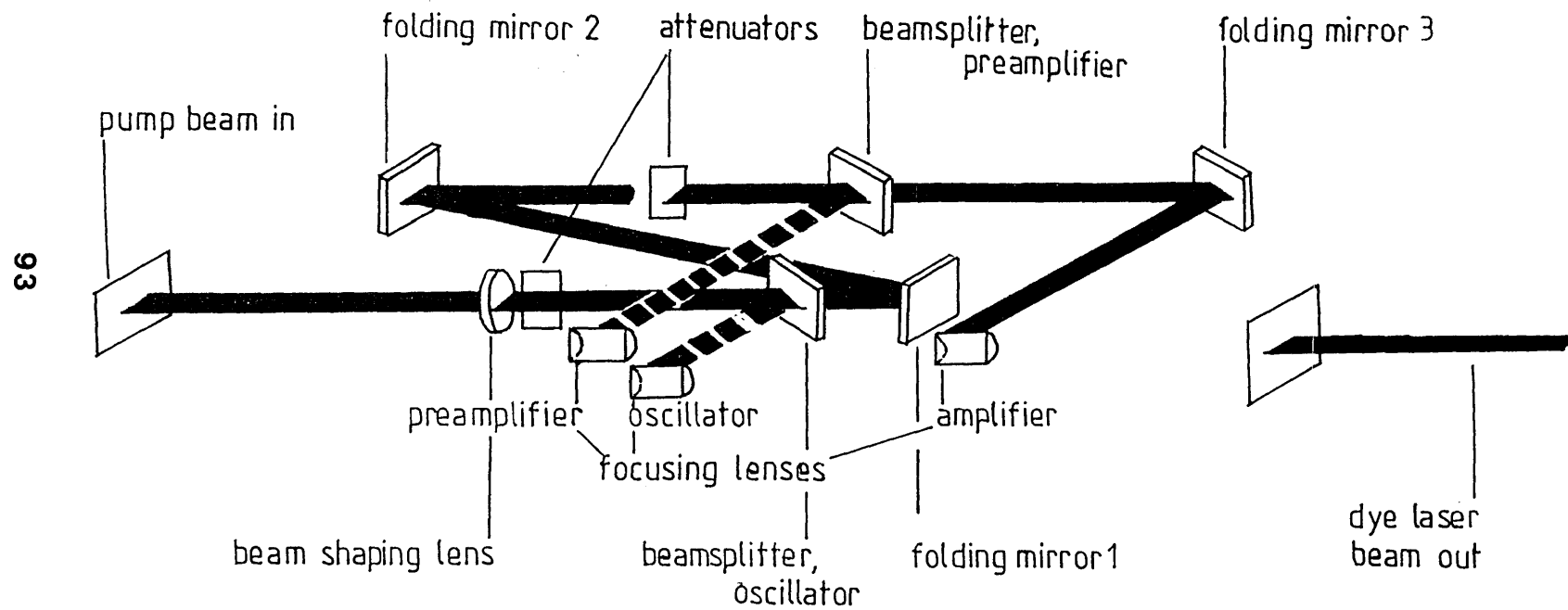
2.2.2b The dye laser

The theory and operation of dye lasers has been well reviewed [31-34]. A description of its operation is given as follows:

The pump beam enters the cabinet from the left as shown in figure 2.9 and traverses a beam shaping lens, the mount also carrying the swing in attenuator no.1. The beam then goes through the oscillator beam splitter where 10% of the beam, predominantly of vertical polarisation, is directed towards the oscillator/preamplifier cuvette. The pump beam hits folding mirror no.1 and is directed to folding mirror no.2, positioning the beam 2.5cm higher. It is reflected and again runs parallel to the 4-rod optical bench. Attenuator no.2 allows attenuation of both pre and main amplifiers.

On the beam traversing the preamplifier beam splitter, 10% of the pump beam is again split off and

Figure 2.9 Diagram of the laser beam path through the dye laser.



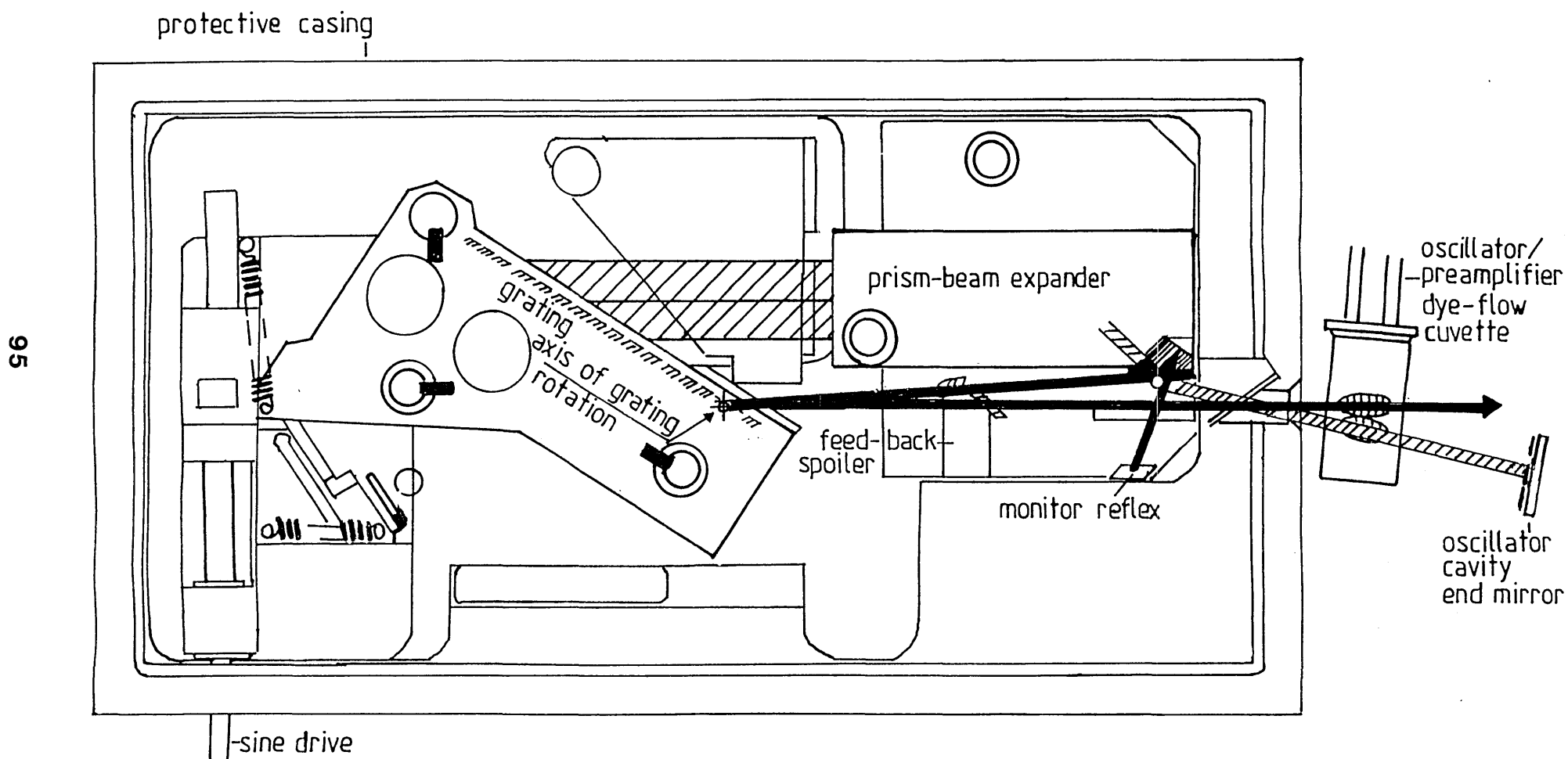
directed towards the preamplifier cuvette, the delay between the pump beam for the oscillator and of the pre and main amplifier being in the order of 4ns. Lastly the beam hits the third mirror and is completely deflected by 90° towards the main amplifier cuvette.

The oscillator and preamplifier pump beams are focused into the dye flow cuvette by cylindrical dye focusing lenses with the focus line close to the pump beam window. The main amplifier is focused behind the cuvette to prevent damaging it.

The tuning block (figure 2.10) is situated on the left hand side of the "4-rod" optical bench and is kept completely enclosed except during alignment. It contains all components which determine the wavelength of the oscillator radiation. The grating ($k = 600$ grooves/mm, 2.7 micron blaze, zero-dur substrate) can be tilted between Littrow angles of 42.5° and 72°. It is used in the third to eight order depending on which dye is selected. The grating is mounted on a Ruby-ball bearing and positioned by means of a precision sine drive with a mechanical spindle of better than 2µm. The lead screw of the sine drive is driven by a stepper motor: a gear box using non-slip belts.

The grating has been precisely aligned with respect to its tilt axis, and the sine drive has been calibrated for a linearity better than 0.3nm/order at

Figure 2.10 Diagram of the laser beam path through the tuning block.



the factory.

The prism beam expander (PBE) consists of a set of five prisms on a common platform. The magnification being 66X. The PBE acts as a 20:1 polariser in favour of vertical polarisation.

The end mirror is located to the right of the flow cuvette crate. There is a mirror carrying three dielectric coatings which covers the end mirror, the chosen coating varying with the chosen dye.

The first part of the oscillator beam path runs between the cavity end mirror, through the dye flow cuvette, and into the prism beam expander. Once inside the PBE the beam is expanded vertically. This beam leaves the expander as a light ribbon following the grating perpendicular to the grooves. For a beam path wavelength matching the Littrow condition:

$$\lambda_0 = 2 (\sin \alpha)/KN \quad (9)$$

light is reflected back, following the incoming path through the beam expander and the pumped region onto the end mirror.

The wavelength is tuned by $\sin \alpha$ and is changed by rotating the lead screw of the sine drive. K is the grating constant of 600 grooves/mm, and n is the grating order in use.

The PBE is required to reduce the bandwidth of the oscillator radiation which is a function of the divergence, $d\alpha$, of the oscillator and the angle, α , determined by the Littrow condition at which the grating is used:

$$d\lambda = d\alpha \lambda / 2 \tan \alpha \quad (10)$$

The PBE reduces the acceptance angle, $d\alpha$, by its magnification, M , $d\alpha = d\alpha M$. Obviously, only a magnification in the plane of diffraction is required.

The output beam of the oscillator is derived from the reflection of the oscillator beam at the entrance prism: 25% of the oscillator beam is split off and routed to the grating and hitting it at the point of rotation, where it is reflected at 4° , back into the oscillator/preamplifier dye cuvette. The grating thus acts as a wavelength selector for the oscillator output and reduces the contribution of the broad-band background fluorescence emitted by the oscillator at the wings of the tuning range. The output beam passes through a set of "spoiling wedges" which disrupt the feedback path between the output portion of the grating and the end mirror, they also have a polarising effect.

The monitor reflex is derived from inside the entrance prism from the beam returning from the grating. It is re-routed via internal reflections and emerges as shown in figure 2.10. It gives a useful

indication of the quality of the beam during alignment.

The bandwidth is specified to be less than 0.2cm^{-1} . The pulse length and pulse form of the dye laser correspond to approximately to those of the excimer laser. Typical operational parameters for the measurement of fluorescence excitation spectra are listed in table 2.1(a).

2.2.2c Second harmonic generation

The study of all the compounds necessitated the use of second harmonic generation (SHG), due to the limitations of the dye laser where the most blue dye used was paraterphenyl (335-350nm). The theory of SHG has been adequately covered [35,36] and will be discussed briefly here.

A radiation of frequency, f , on passing through certain crystal media will emerge as a mixture of two frequencies, the original frequency, f , and a new frequency, $2f$. This is a so called non-linear effect that has only been observed due to the advent of high power densities of lasers [37]. The crystal consists of atoms whose nucleus and associated electrons form electronic dipoles. The interaction of electromagnetic radiation with these dipoles causes the dipoles to act as a source of electromagnetic radiation. If the amplitude of their vibration is small, they emit the same incident radiation. However, as the intensity of the incident

Table 2.1 Typical experimental parameters for the measurement of fluorescence excitation spectra.

a) Excimer-pumped dye laser

Excimer	XeCl
Energy/pulse (excimer)	100mJ/pulse
Pulse length	17ns
Wavelength	308nm
Repetition rate	20Hz
Dye	Rhodamine 6G
Energy/pulse (dye)	12mJ/pulse
Pulse length	17ns
Frequency	570-610nm
Energy/pulse (U.V.)	~1mJ
Frequency	285-305nm
Frequency stability	< 0.05cm ⁻¹
Wavelength reproducibility	+ 4.4Å

b) Boxcar averager

	Averaging unit	
	A (fluorescence)	B (laser intensity)
Trigger	external	external
Delay	1ns	1ns
Width	30ns	30ns
Signal sensitivity	0.2V	50mV
Averaging samples	10	10

radiation increases so does the amplitude of vibration of the dipole. For a large amplitude the non-linearities become apparent. The result is that the frequency of oscillation of the dipole has harmonics, the strongest harmonic being at twice the frequency of the incident radiation.

If the strength of the dipoles is defined by P (polarisation) and an applied electric field by E then it is shown that:

$$P = X_1 E + X_2 E^2 + X_3 E^3 + \dots \quad (11)$$

X = polarisability

If E takes the form of an oscillating field $E = E_0 \sin(ft)$, such as produced by an electromagnetic wave, then substitution gives:

$$P = X_1 E_0 \sin(ft) + 1/2 X_2 E_0 (1 - \cos 2ft) + \dots \quad (12)$$

(12) contains a term in $2f$ which corresponds to an electromagnetic wave having double the frequency of the incident wave.

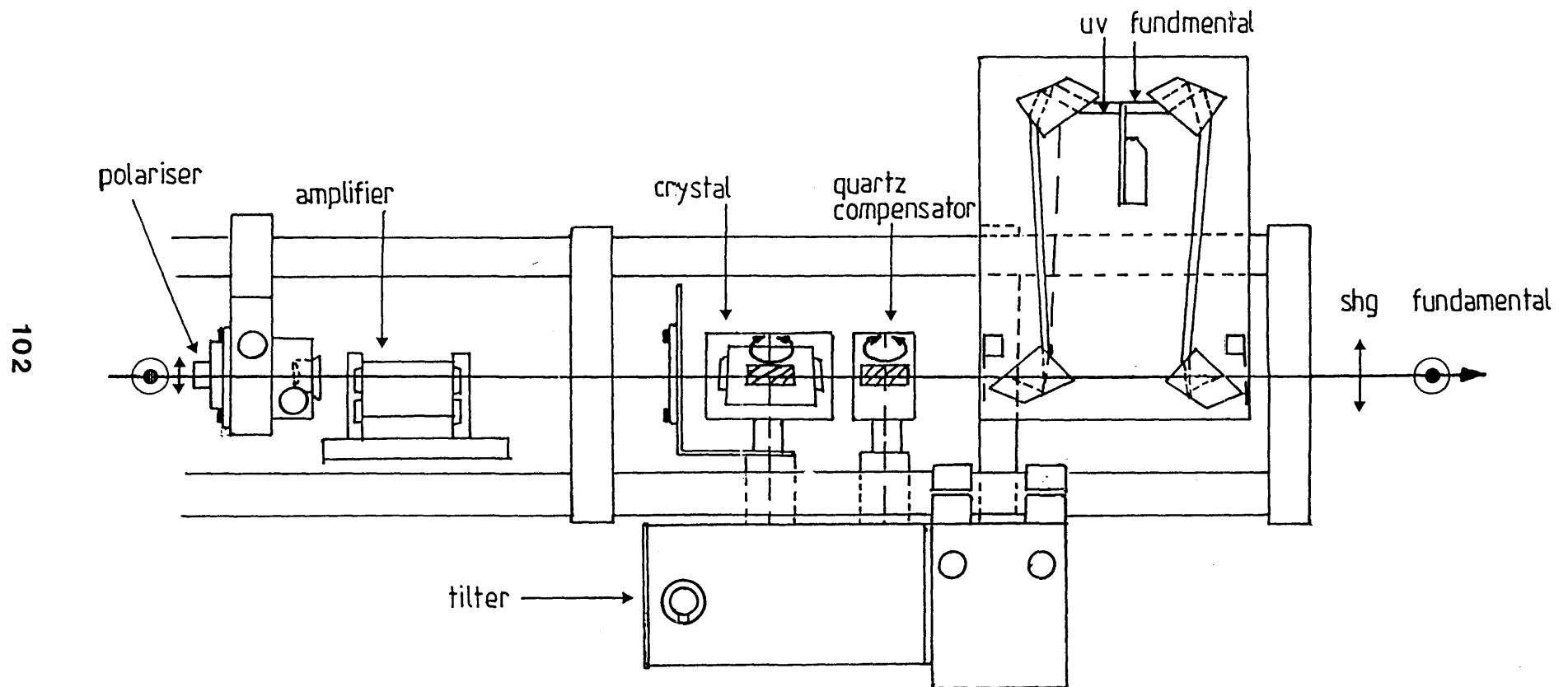
Not all solids exhibit frequency doubling. If the material has a centre of symmetry then, an applied electric field must produce polarisation of the same magnitude but of opposite sign according to whether the applied field is positive or negative. Hence, for materials with such a centre of symmetry such as glasses and liquids the coefficients $X_2, X_4, \dots$ etc must all be

zero. As X_2 is zero no frequency doubling is observed.

SHG produces a wave that is orthogonal to the incident wave, hence, the light at twice the frequency will exist as a beam which is independent of the angle of the crystal. By altering the angle of the crystal it is possible to match the refractive index of the light at the fundamental frequency, f , to the light at $2f$ whose refractive index remains constant. By index matching, the two rays are phase matched and so destructive interference does not occur and SHG propagates through the entire crystal.

SHG for the FL2002 dye laser is shown in figure 2.11. A polariser was placed in front of the amplification stage to produce parallel polarisation. The FL 30 crystal (range 540-700nm) is mounted in a hermetically-sealed housing unit with accompanying temperature stabilisation. Automatic beam displacement correction is achieved with a quartz compensator (qc) which synchronously rotates in the opposite direction to the crystal. This is accomplished by using the Lambda Physik FL 582 microcomputer which contains an angle wavelength trajectory for the crystal. The program allows the computer to adapt the stored parameters to the working conditions of the dye laser. Before starting the first scan, the crystal is moved after prompting from the FL 528 to various positions to generate second harmonic output, over the required

Figure 2.11 Diagram for the set up of second harmonic generation in the dye laser.



tuning range. At each position, the second harmonic output is maximised. This is fed into the computer where the exact trajectory is determined via a polynomial fit. The crystal tracking then becomes completely automatic. The set up of the crystal and the qc had to be carried out each time the crystal was removed. The initial set up was achieved by having the beam going through both crystal and qc without deviation from the original path. The laser beam is attenuated at this stage in order to prevent damage to the crystal. A simple procedure set out by the wavelength control program was followed in order to find $2f$ using a red filter placed directly after the qc. On having completed the set up the red filter was removed and separation of the fundamental and the second harmonic was achieved using the Lambda Physik FL35. This consists of 4 Pellin-Broca prisms almost set to Brewster-angle (figure 2.11) dramatically reducing losses, including those obtained from reflection losses, compared to using a red filter. The SHG was approximately of 10% efficiency.

2.2.3 The photomultiplier tube

The photomultiplier (pm) tube outputs an electrical pulse when a photon strikes the photo cathode, though it does not emit a pulse every time due to the quantum efficiency of the photocathode being less than unity. Adjustment of the voltage divider chain was made to maximum sensitivity. The pm tube used for detecting

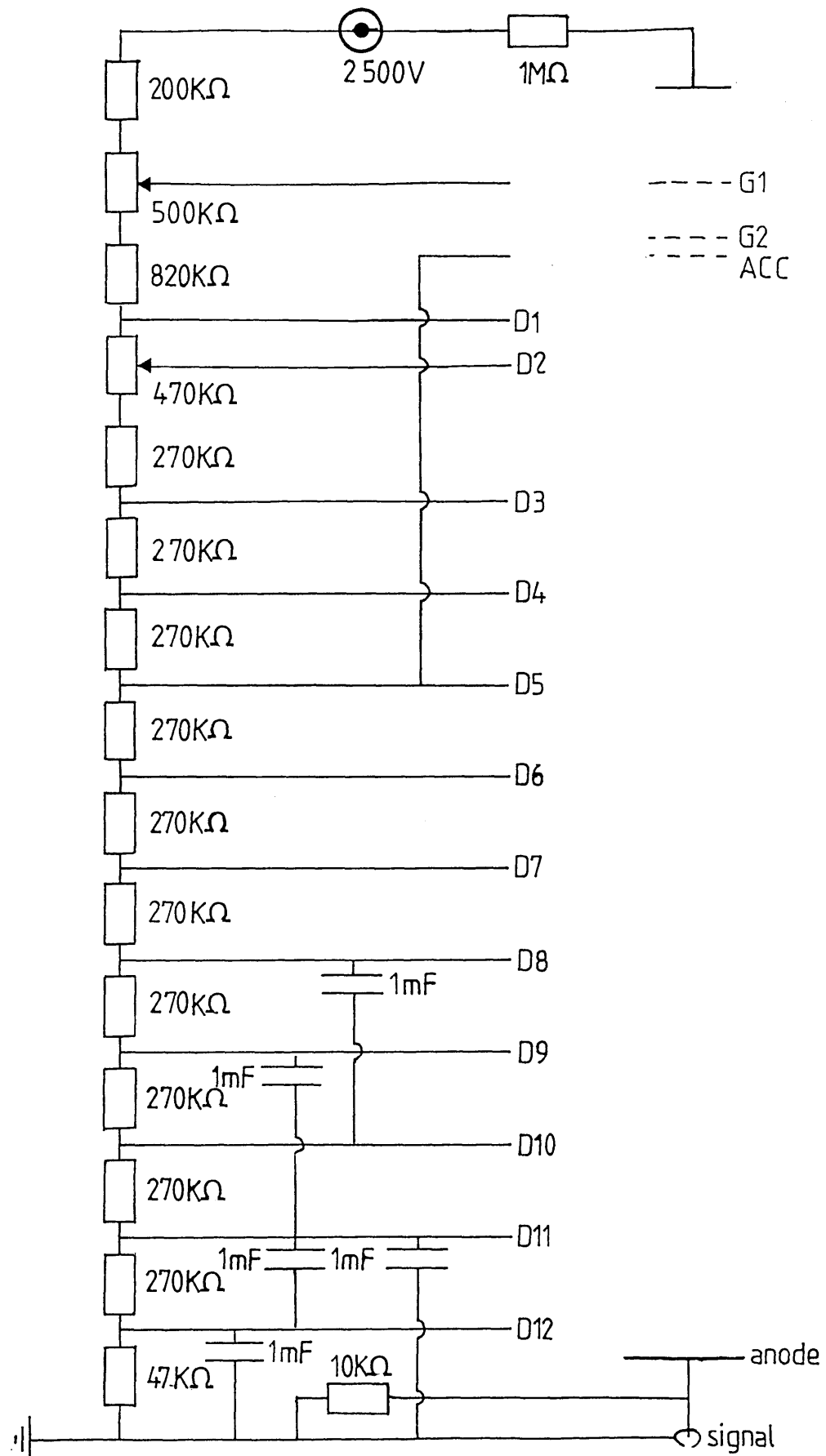
excitation spectra was the EM1 XP2020 Q PAT, the dynode chain for which is shown in figure 2.12.

2.2.4 The gated integrator and boxcar averager

The SRS (Stanford Research Systems) model SR250 gated integrator and boxcar averager allows the recovery of fast analogue signals from noisy backgrounds. The SR250 consists of a gate generator, a fast gate integrator and exponential averaging circuitry. The gate generator, triggered internally or as in our case externally from the synchronous output of the excimer laser provides an adjustable delay from a few nanoseconds to 100 milliseconds before it generates a continuously adjustable gate of 2ns to 15ms. The delay is set by a front panel potentiometer. The fast gated integrator integrates the input signal during the gate. The output from the integrator is then normalised by the gate width to provide a voltage which is proportional to the average of the input signal during the sampling gate. This signal is further amplified by a front panel sensitivity setting. A moving exponential average over 1-10,000 samples is available at the "averaged output". The averaging technique is useful for pulling small signals from noisy backgrounds. On averaging, many noisy samples of a signal, the average will emerge to the mean value of the signal and the noise will average to zero.

In our experiments, two SR250 gated integrator

Figure 2.12 Circuit diagram of the dynode chain of the EMI XP2020 Q photomultiplier tube.

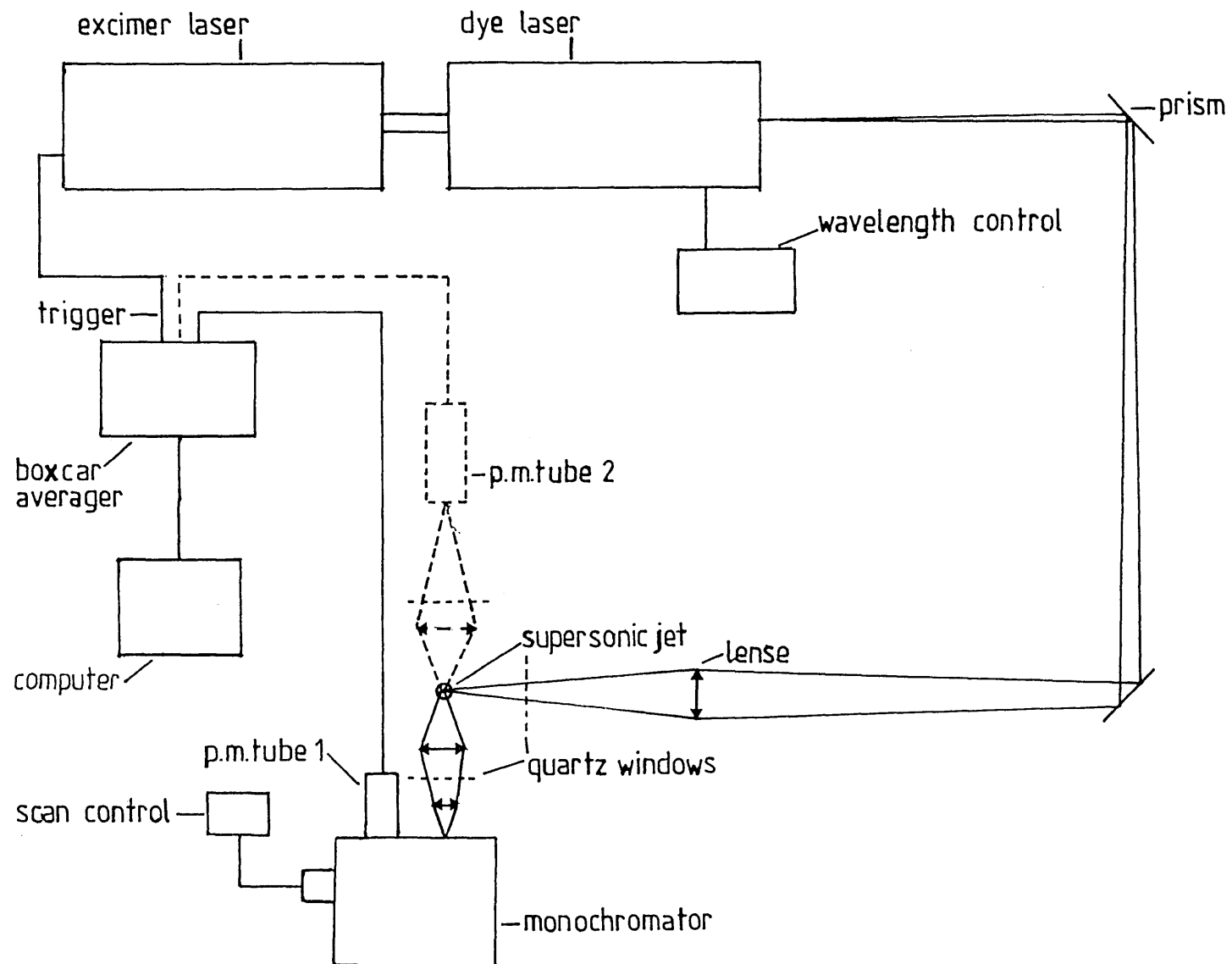


averager units are used; one to monitor variation in fluorescence from sample on changing excitation frequency or in dispersed fluorescence and the other to monitor the variation in laser intensity over the dye tuning range and/or drop off in laser intensity with time. By using the rationing setting on the analogue processor, the variations can be compensated for and, hence, normalised relative intensity across the spectrum was obtained. Typical operational parameters are listed in table 2.1(b).

2.3 THE MEASUREMENT OF DISPERSED FLUORESCENCE SPECTRA

The apparatus used for recording dispersed fluorescence spectra is shown in figure 2.13. In this case, the exciting wavelength is fixed at a particular absorption wavelength of the molecule and the emitted light is dispersed with a monochromator. The monochromator was the Rank Hilger Monospek 1000 fitted with 2400 lines per mm holographic grating with reciprocal dispersion of $8\text{\AA}$ per mm. It was driven by a stepper motor, Sanyo Denki 103-770-2, giving accurate 1.8° turns to the grating drive. Using the 2400 lines per mm grating gives the equivalent to a step of $0.0625\text{\AA}$ approximately a step of 0.54cm^{-1} in the 340nm wavelength region. The power supply and logic signals were controlled by a home-made unit driving a Walter James, WJ01, control board. Timing pulses were

Figure 2.13 Diagram of the apparatus used to measure dispersed fluorescence spectra.



originally obtained from a preset counter/timer (Canberra 1770). On the purchase of an ARC Turbo-8 microcomputer the timing pulses were obtained from this.

Resolution was limited by the slits to approximately 5cm^{-1} FWHM [11]. Calibration of the monochromator was originally made using an Iron Neon Hollow cathode (INHC) lamp, cathodeon 3QNY/Fe. The excimer pumped dye laser, which had a bandwidth of 0.2cm^{-1} FWHM, was used for calibration of the monochromator following installation.

Instead of using a split off from the laser beam to monitor fluctuation in laser intensity while recording dispersed fluorescence spectra the total unresolved fluorescence was used as a standard. The laser excited fluorescence was focused at the monochromator slits and the dispersed output was detected using a PMT, Hamamatsu R928. Space restrictions required the use of a side-on PMT with a special base wiring [38]. The recording of the spectra was as described for excitation spectra in section 2.2.

2.4 THE MEASUREMENT OF FLUORESCENCE LIFETIMES

A simple kinetic scheme gives the definition of the quantum yield of fluorescence, Φ_f , and fluorescence decay time, τ_f , in terms of first order rate constants. A steady state analysis gives:

$$\Phi_f = k_r / (k_r + k_{nr}) \quad (13)$$

k_r = radiative rate-constant

k_{nr} = non-radiative rate-constant

The fluorescence lifetime is an experimental observation and is given by:

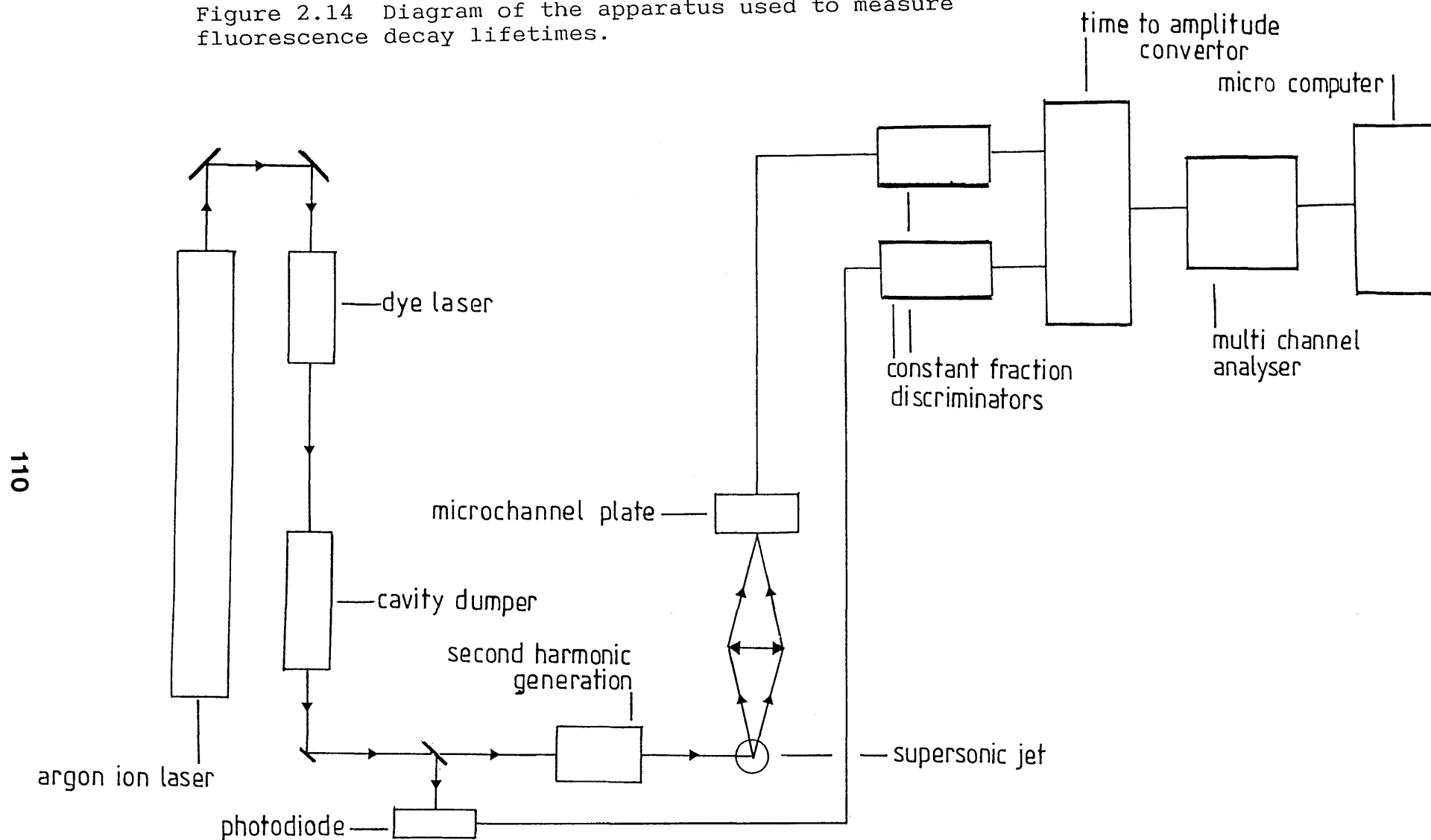
$$\tau_f = (k_r + k_{nr})^{-1} \quad (14)$$

There are many contributions to k_{nr} many of which having been studied in the jet [11, 39-45]. Only a brief description of the measurement of fluorescence lifetimes. A full account may be found in reference [46]. The lifetimes were determined using the technique of time correlated single photon counting.

The single photon counting measurement relies on the concept that the probability distribution for emission of a single photon after an excitation event yields the actual intensity against time distribution of all the photons emitted as a result of the excitation. By sampling the single photon emission following a large number of excitation flashes, the experiment constructs the probability distribution.

As shown in figure 2.14, part of the pump beam (actually a reflection of the SHG crystal face) is detected by a photodiode and is used as a trigger. The trigger pulse is routed through the constant fraction

Figure 2.14 Diagram of the apparatus used to measure fluorescence decay lifetimes.



discriminator (Ortec 584) to the stop pulse of the time to amplitude converter (Ortec 457) which initiates the charging of a capacitor. The signal resulting from one fluorescence photon from each excitation event is used to start the charging ramp in the time-to-amplitude convertor (TAC) which puts out a pulse the amplitude of which is proportional to the charge in the capacitor and hence to the time difference between start and stop pulses. The TAC output pulse is given a numerical value in an analogue to digital converter and a count is stored in the data storage device (multi-channel analyser) in an address corresponding to that number. Excitation and data storage are repeated in this way until the histogram of number of counts against address number in the storage device represents, to some required precision, the decay curve of the sample.

2.4.1 The excitation source

Fluorescence lifetimes were obtained using the frequency-doubled output of a synchronously pumped, mode-locked, cavity-dumped dye laser as the excitation source. The system has previously been described at length [47,48] and only a brief description will be given here.

2.4.1b Mode-locked ion laser

Population in the dye laser is achieved by optical pumping with the mode-locked argon-ion laser,

Spectra-Physics 171, the lasing medium in the argon-ion laser being the excited state of the Ar^+ ion which is created by a continuous electrical discharge through argon gas contained in the plasma tube. Stable mode locking of the laser is achieved [35,48] by the accurate fine adjustment of the cavity length in order to match the cavity round trip time to the modulation frequency of the mode locking crystal. The crystal has a preferred resonant frequency for each temperature setting and amplitude of the applied rf signal. The output power of the laser beam was maximised using angular adjustments of the end mirrors.

2.4.1b The dye laser

The length of the dye laser was adjusted to match that of the ion laser in order to achieve synchronous pumping. This resulted in the mode locking of the dye laser with the mode separation being equal to that of the ion laser. However, the gain bandwidth of the dye laser allows many more modes to lase. This, coupled with higher cross section for stimulated emission of the organic dye, produces pulses in the cavity which are approximately ten times shorter than the exciting ion laser's pulses. The original wedge tuning element was replaced by a two plate birefringent filter taken from a Coherent dye laser coherent 590-03 [11]. The intra cavity pulse repetition rate of the dye laser was the same as that of the ion laser, that is, 82MHz.

An interpulse separation of only a few nanoseconds is unsuitable for lifetime measurements [49], except in the excitation of very short-lived samples [50]. By using a Spectra physics Model 344 acousto-optic cavity-dumper the interpulse separation can be varied. The cavity dumper employs the interaction of light with a moving sound wave [51] to produce a time dependent diffraction effect.

Table 2.2 Operational parameters for the mode-locked ion pumped dye laser system.

	Mode-locked ion laser 514.5 nm	Output dye laser (Rhodamin 6G dye) 595 nm
Average power	750 mW	60 mW
Pulse width FWHM	180 ps	10 ps
Repetition rate	82 MHz	4 MHz (max) one shot (min)

2.4.2 Second harmonic generation (see section 2.2.3)

SHG was carried out using a KDP crystal (figure 2.14). A 10cm focal length lens was placed before the crystal to focus the laser beam to a waist. The light was recollimated after using another 10cm lens after passing through the KDP crystal before passing

through a filter (Corning 7-54) which removed the fundamental beam. A variable half-wave plate was placed before the crystal to rotate the plane of polarisation of the laser light from the vertical to the horizontal. The second harmonic was generated by tuning the angle of the crystal in the vertical plane containing the optical axis.

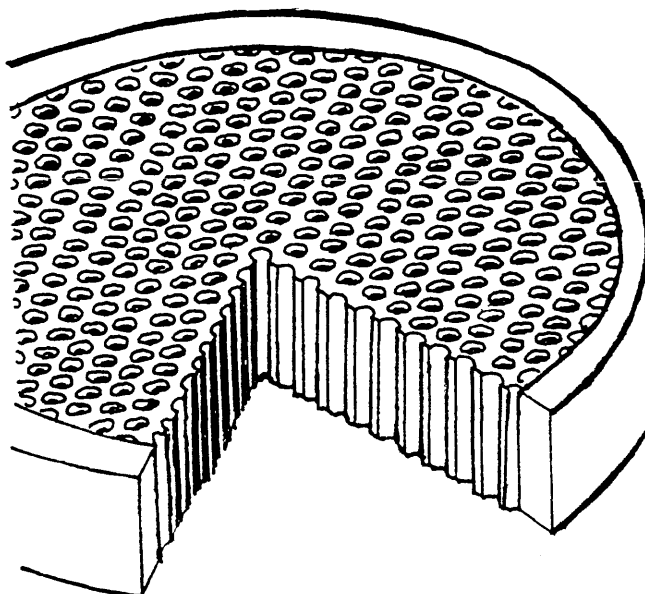
2.4.3 The micro-channel plate photomultiplier tube

The micro-channel plate photomultiplier tube (MCP) is a secondary electron multiplier [52,53] and is a thin plate consisting of a bundle of millions of very small glass capillaries (figure 2.15a) or channels with internal diameters 10 μ m to 20 μ m. These capillaries are fused into the form of a thin (1mm) disc and the inside walls are coated with a secondary electron emissive material. Both ends of the channel are covered with a thin metal film which acts as the electrode. Each of the capillaries acts as an independent electron multiplier giving 10⁴ electron gain under 1 KV applied voltage between both sides of the capillaries [54]. A schematic representation of electron amplification in a single channel is given in figure 2.15b.

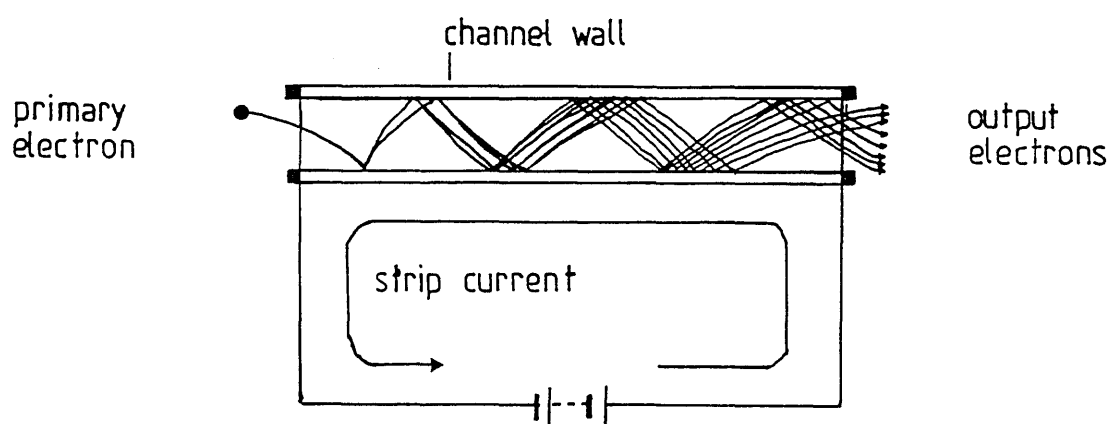
A MCP has the advantage of an extremely fast time response with a very small transit time spread and good single photon resolution can be achieved. It is also subject to very small or negligible wavelength

Figure 2.15 a) Diagram of a microchannel plate. b) Schematic representation of electron amplification of a single electron.

a)



b)



effects [52].

There are some drawbacks with ion feedback causing reduced photocathode lifetime and after pulsing. Also, a reduced counting rate resulting from the "bad time" required to neutralise the residual positive charge remaining in the channel after the passage of an electron current [46]. In this experiment a response function of 140ps FWHM was achieved with a Hamamatsu R1564U-01 micro-channel plate photomultiplier tube. This enabled the calculation of lifetimes without convolution with the instrument response function.

2.5 EXPERIMENTAL DETAILS

Listed in table 2.3 are the details of the compounds and solvents studied. The sample vapour was mixed with helium carrier gas at stagnation pressures of 3-4Bar and allowed to expand through the continuous flow nozzle with diameter of 97 or 108 μ m. The solvent was introduced into the expansion by diverting a controlled fraction of the carrier gas through the resevoir containing the solvent at room temperature.

Table 2.3 Source of a) compounds and b) solvents used in this research.

a)

compound	source	oven temperature. °C
4-N,N-dimethyl-aminobenzonitrile	Aldrich Ltd	104
N,N-dimethylaniline	"	45
4-aminobenzonitrile	"	100
N-methylaniline	"	45
3-aminobenzonitrile	"	110
2-aminobenzonitrile	"	105

b)

solvent	source
methanol	BDH
ethanol	"
propan-1-ol	"
butan-1-ol	"
chloroform	"
acetonitrile	Aldrich Ltd
propionitrile	"
i-butyronitrile	"

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CHAPTER 3

SPECTROSCOPY OF 4-N,N-DIMETHYLAMINOBENZONITRILE AND ITS
VAN DER WAALS COMPLEXES: THE ABSENCE OF THE TICT STATE

CHAPTER 3

SPECTROSCOPY OF DMABN AND ITS VAN DER WAALS COMPLEXES: THE ABSENCE OF THE TICT STATE

3.1 INTRODUCTION

As discussed in Chapter 1, much interest has been generated in 4-N,N-dimethylaminobenzonitrile (DMABN) and like molecules because of their unusual fluorescence properties. In polar solvents, DMABN exhibits an anomalous a^* emission red-shifted from the normal b^* fluorescence. Despite numerous experiments carried out in the solution phase [1] the role of the solvent molecules in assisting the formation of the a^* state is not completely understood (Chapter 1 section 1.3). The development of the supersonic jet (Chapter 2 section 2.1) and subsequent understanding of microscopic solvent effects [2] provides a useful technique to study the role of the solvent molecules in assisting the formation of the a^* state.

Time-resolved fluorescence measurements [3] show that the kinetics of formation of the a^* state in solution are complicated and, as yet, inadequately described. The picosecond measurements of Wang and Eisenthal [4] suggested that the formation of a^* state is facilitated by ground state DMABN-solvent (in this case, butan-1-ol) complex formation. It might, therefore, be supposed that the a^* fluorescence could be produced under

jet-cooled conditions. Kobayashi et al [5] recently reported the absence of a^{*} fluorescence from jet-cooled complexes of DMABN with water and trifluoromethane. Absence of excitation features corresponding to complexes of higher than 1:1 stoichiometry was also reported. In this chapter, similar behaviour for DMABN-alcohol complexes is reported. It is suggested that this behaviour is due to the formation of a non-emissive a^{*} state.

Despite the numerous publications on DMABN in the solution phase, very little work has been carried out which contributes towards the understanding of the spectroscopy of the molecule. The little vibrational work undertaken is minimal [6] or inconclusive [7] because of the complicated nature of the molecule, in particular the amino group. DMABN is found to be planar in the ground state [8] and hence belongs to the C_{2v} point group [9]. Many INDO type calculations have been conducted on the singlet states [10-13] of DMABN. Those carried out by Lipinski et al [10] reveal that the lowest energy transition is to the ¹B₂ singlet state and that the planar structure is most stable in the ground and excited state both in the gas phase and in solution which is experimentally supported (see Chapter 1). From the results presented here, there appears to be a change in geometry in the excited state some of which is attributed to torsion of the amino group though not to the full

extent required for a* emission.

Another phenomenon which has to be considered is the inversion undergone by the amino group. A smaller pyramidal angle is envisaged in aromatic amines than aliphatic amines accompanied by a smaller barrier to inversion [14,15] as found in aniline. The effect of para-substitution with an electron acceptor is thought to lower this barrier further. The inversion of the amino group is discussed more thoroughly in Chapter 4 where it becomes more apparent for the molecule 4-amino-benzonitrile.

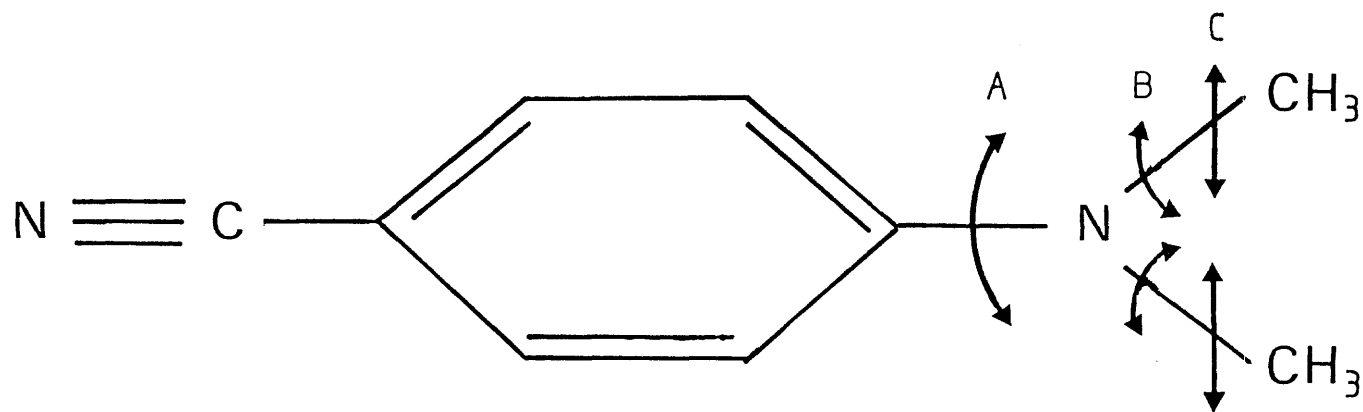
Figure 3.1 illustrates the oscillations of the amino group that have to be considered in order to interpret the complicated nature of the observed spectra.

3.2 EXPERIMENTAL

DMABN was obtained from Aldrich ltd and used without further purification. The sample vapour (produced by heating the solid to 104°C) was mixed with helium carrier gas at stagnation pressures of 3-4 Bar and allowed to expand through the continuous flow nozzle with diameter of 108µm diameter. All solvents used were spectra grade and obtained from BDH. Other experimental details are found in Chapter 2.

Figure 3.1 Possible modes active in the ground and excited states of DMABN.

- A = Aryl—N torsion
B = N—CH₃ torsion
C = N inversion



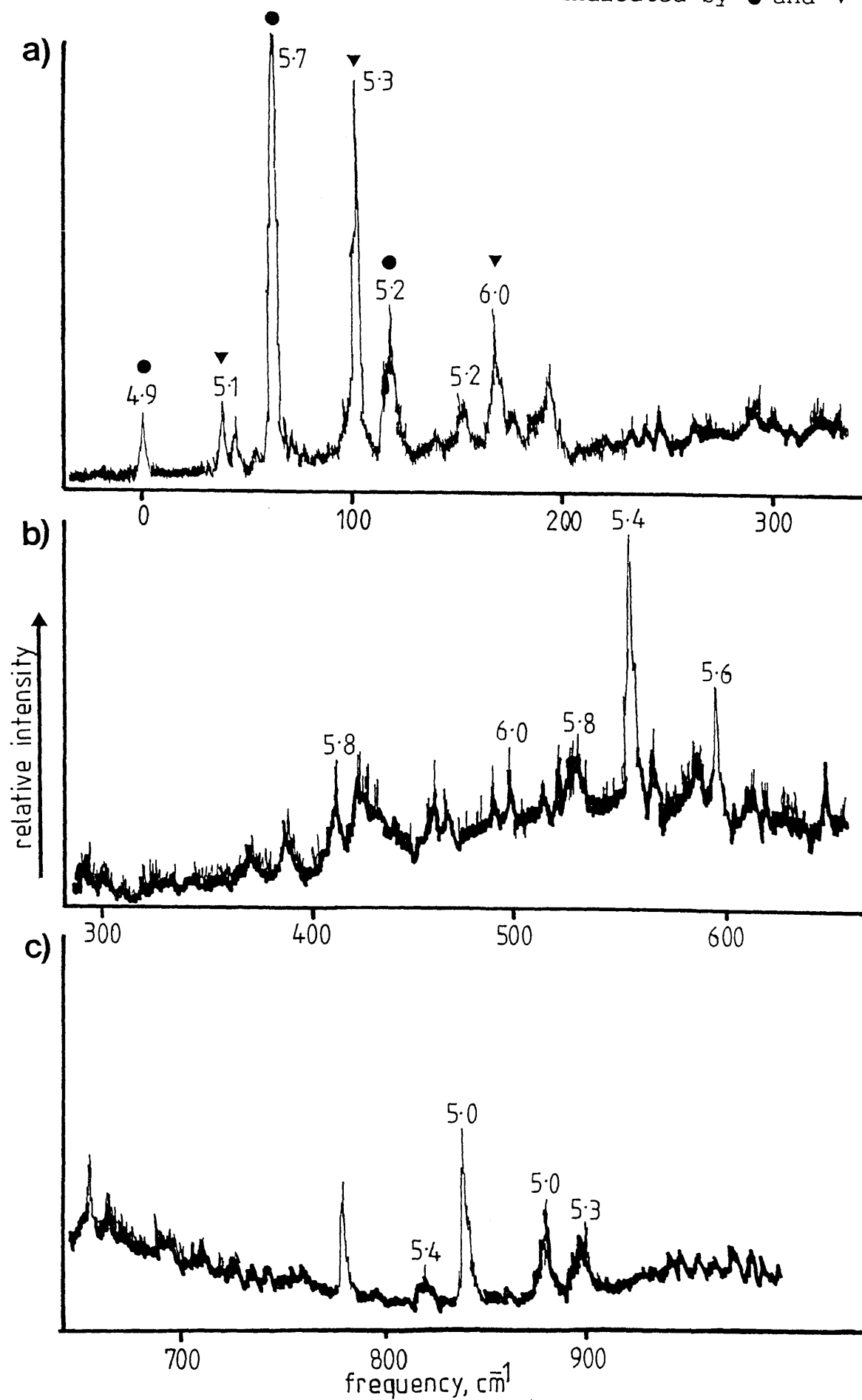
3.3 RESULTS

3.3.1 Excitation spectrum of DMABN

The fluorescence excitation spectrum of jet-cooled DMABN is shown in figure 3.2 and is in good agreement with that recently reported by Kobayashi et al [5]. The lowest energy transition occurs at $32,333\text{cm}^{-1}$. The characteristic pattern of low frequency transitions observed in the origin region appears to consist primarily of six bands with frequencies progressing from the lowest energy transition 0_0^0 , 37cm^{-1} (a_0^1), 42cm^{-1} (b_0^1), 61cm^{-1} (c_0^1), 99cm^{-1} (d_0^1) and 117cm^{-1} (e_0^1). Two progressions can be obtained in 61cm^{-1} these being highlighted by figure 3.2a. The fluorescence excitation spectrum of DMABN is complicated because of the various oscillations of the molecule as illustrated by figure 3.1. These low frequencies modes can be attributed to the torsion of the amino group around the N-aryl bond, torsions of the CH_3 groups and the pyramidal inversion of the amino nitrogen (for an in depth discussion of the inversion of the amino nitrogen see Chapter 4). The torsional frequencies are comparable in magnitude to:

(1) The frequencies found for torsions of the amino group in the far infrared spectrum of N,N-dimethylaniline (DMA) vapour were of the order of 66cm^{-1} and 117cm^{-1} [16]. These were assigned to the three torsions $\text{N}\ddagger(\text{CH}_3)_2$ and $\text{C}_6\text{H}_5\ddagger\text{N}(\text{CH}_3)_2$ though there was no direct assignment of

Figure 3.2 Fluorescence excitation spectrum of DMABN. Two frequency progressions of 61 cm^{-1} are indicated by $\bullet$ and $\blacktriangledown$.



the frequencies because of the complicated nature of the molecule.

(2) Further work carried out on DMA under supercooled conditions. The fluorescence excitation spectrum can be seen in figure 3.3. It exhibits the same frequency patterns as DMABN but appears to be more complicated. The relative quantum yield appears to be an order of magnitude lower also. The spectroscopy of DMA is discussed in more detail in Chapter 5.

(3) Theoretical calculations using a molecular force field program [17] which calculated low frequency modes for DMA and 4-N,N-dimethylaminobenzaldehyde (DMABA). The latter are listed in table 3.1. DMABA has a stronger electron accepting group (-COOH) than DMABN (-CN) and so frequencies would be expected to lie between those for DMABA and DMA.

The distinctive pattern of six bands recurs three times in the spectrum, this being most clearly illustrated by figure 3.2c where the final set of transitions progressing from 780cm^{-1} greatly resembles the origin region. The other two are indicated in Table 3.2. The recurring pattern is built on fundamental vibrations of the benzene ring; starting frequencies being 373cm^{-1} (ν'_1), 494cm^{-1} (ν'_2) and 780cm^{-1} (ν'_3). Comparison with the electronic absorption spectrum of 4-aminobenzonitrile (4-ABN) [18] and with the fluorescence

Figure 3.3 Fluorescence excitation spectrum of N,N-dimethylaniline.

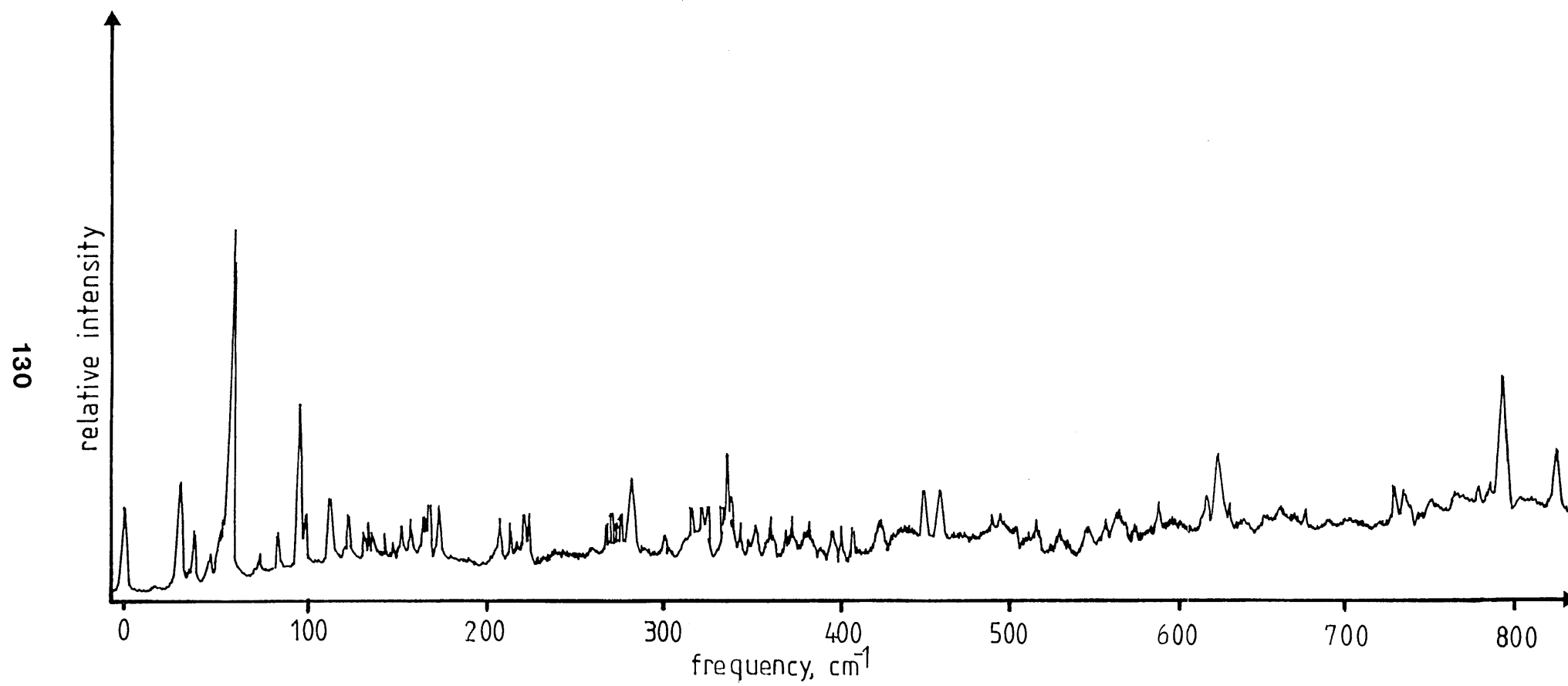


Table 3.1 Calculated ground-state low-frequency normal modes of N,N-dimethylaniline (DMA) and 4-N,N-dimethylaminobenzaldehyde (DMABA).

	DMA frequency, cm^{-1}	DMABA	assignment
A	35-50	15-50	$\text{N}(\text{CH}_3)_2$ -twist (and CH_3 rotation)
B	65-80	65-75	$\text{N}(\text{CH}_3)_2$ pyramidal
C	115-130	105-110	CH_3 -rotation
D	120-140	110-120	CH_3 -antirotation
E	240-250	170-185	?
F	260-275	210-230	strongly mixed mode containing pyramidal twist, CH_3 -rotation and ring deformation

Table 3.2 Assignments and fluorescence lifetimes, τ_f , of the fluorescence excitation spectra of DMABN. Frequency values are accurate to $\pm 2\text{cm}^{-1}$ and τ_f to $\pm 5\%$.

Frequency (cm^{-1})	relative intensity	τ_f (ns)	assignment
0	15	4.9	0_0^1
37	11	5.1	a_0^1
42	8		b_0^1
61	100	5.7	c_0^1
97	6		
99	65	5.3	d_0^1
114	12		
117	23	5.2	f_0^1
151	9		
166	20	5.2	e_0^1
193	13	6.0	
251	7		
292	7		
373	8		$6a_0^1$
386	11	5.8	
411	16		$6a_0^1a_0^1$
428	16		$6a_0^1c_0^1$
457	16		
494	16	6.0	$10b_0^2$
532	11	5.8	$10b_0^2a_0^1$
555	48	5.4	$10b_0^2c_0^1$
595	21	5.0	$10b_0^2d_0^1$
615	15		$10b_0^2e_0^1$
651	14		
780	17		1_0^1
818	5		$1_0^1a_0^1$
823	6		$1_0^1b_0^1$
840	25	5.0	$1_0^1c_0^1$
880	14	5.0	$1_0^1d_0^1$
898	9	5.3	$1_0^1e_0^1$

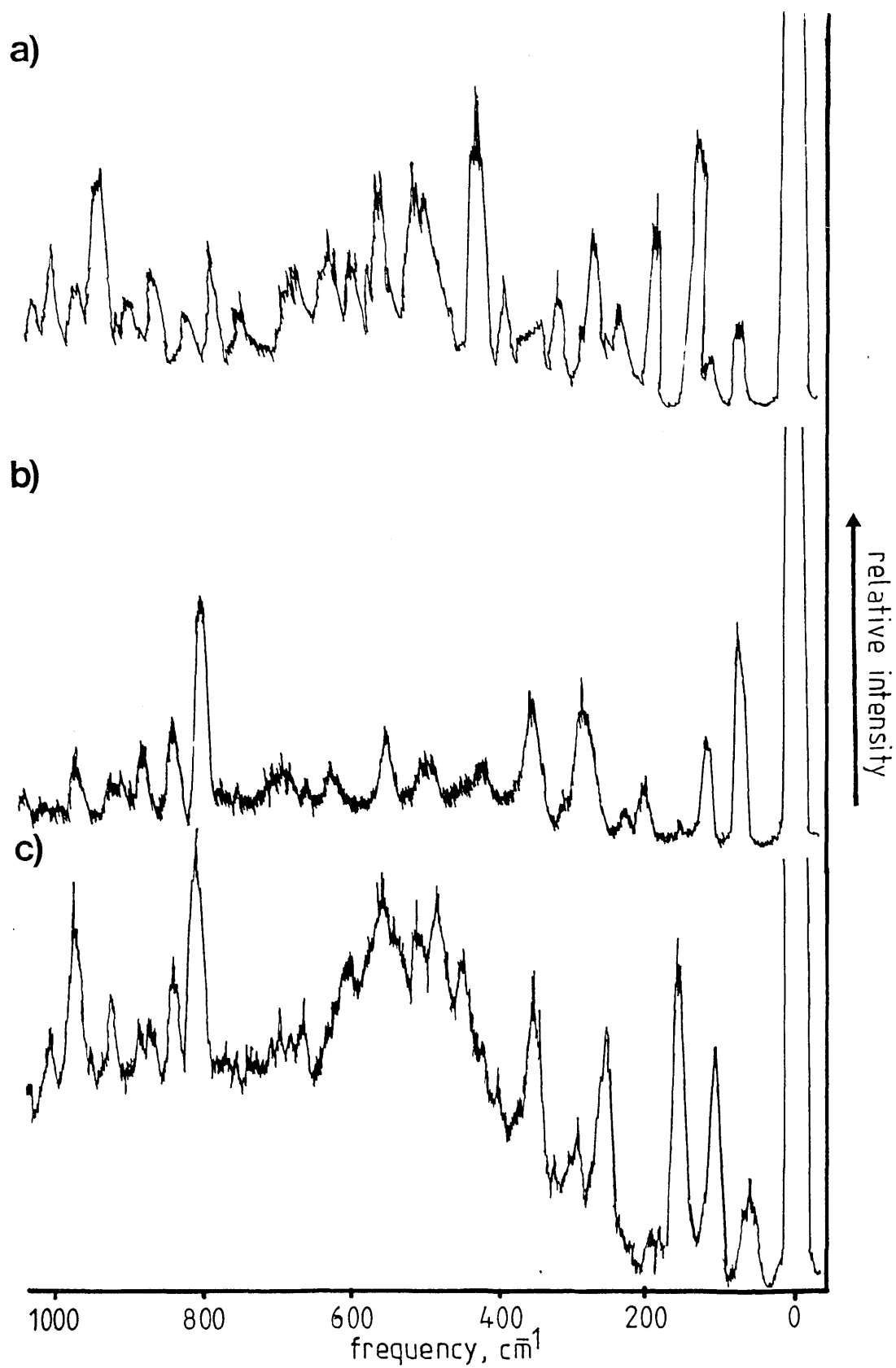
excitation spectrum of jet-cooled 4-ABN (Chapter 4) allows ν_1' to be assigned to the ring deformation mode of benzene (Chapter 1 section 1.6). The 494cm^{-1} , ν_2' , transition corresponds to the C-H bending out of plane mode, 10b. The 780cm^{-1} transition agrees closely with the 778cm^{-1} transition of 4-ABN and has been assigned to the ring breathing mode 1. Two satellite transitions were observed to the blue of c_0' and d_0' at **65** and **104** cm^{-1} respectively. These are thought to be due to internal rotations of the methyl groups [19].

3.3.2 Dispersed fluorescence spectra of DMABN

The dispersed fluorescence spectrum obtained by exciting the lowest energy absorption band is shown in figure 3.4a (the intensity of the resonance fluorescence consists of approximately 75% scattered laser light). There are two routes by which the origin, 0_0^0 , may be characterised:

(1) Comparison of the intensities in the dispersed fluorescence spectrum 3.4a with the fluorescence excitation spectrum 3.2 suggests that the lowest energy transition (y_0') is the first member of a low frequency progression rather than the 0_0^0 transition. The first vibronic transition occurs at $72 \pm 6\text{cm}^{-1}$ compared with 37cm^{-1} in the excitation spectrum. If this band is taken as a false origin then the fluorescence spectral profile in the low energy region corresponds to the

Figure 3.4 Dispersed fluorescence spectra of DMABN following excitation into: a) O_0^0 , b) 61 cm^{-1} and 99 cm^{-1} modes.



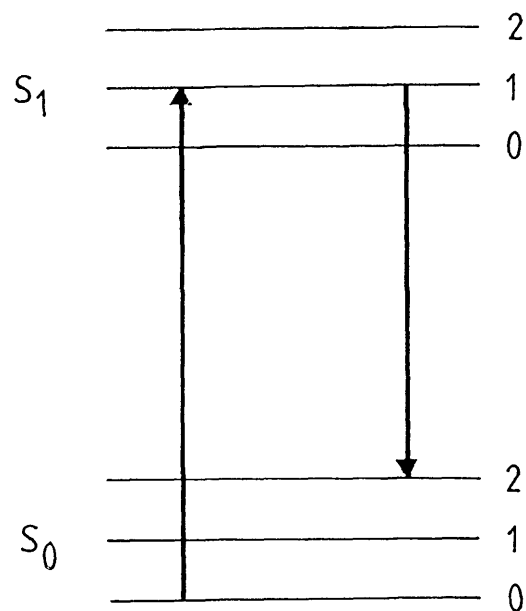
characteristic patterns seen in the excitation spectrum. This implies that the origin of the excitation spectrum corresponds to a $\Delta v = +1$ transition to $v' = 1$ of the 37cm^{-1} (or 42cm^{-1}) mode with the 72cm^{-1} fluorescence band being the $\Delta v = +1$ transition to the $v'' = 2$ level. The 0_0^0 excitation is apparently too weak to observe and the $\Delta v = 0$ transition is absent from the fluorescence spectrum. This is illustrated in figure 3.5a. The origin region of all three spectra shown in figure 3.3 can be assigned by analogy with the excitation spectrum in terms of two frequencies $38 \pm 5\text{cm}^{-1}$ (a_0^1/b_0^1 being unresolved at this resolution) and $70 \pm 8\text{cm}^{-1}$ (c_0^1).

(2) Conversely, if the first transition in the excitation spectrum is indeed due to the 0_0^0 transition other than to internal rotation [5] then the corresponding energy diagram in figure 3.5b demonstrates the resultant normal transitions. Though the intensities do not then correlate they may be accounted for by the fact that differing oscillations of DMABN maybe more dominant in the ground state than in the excited state. An attempt can be made at assigning the ground state frequencies as shown in table 3.3 though this is hampered by the abundance of low frequency modes coupled with the limited resolution of the monochromator (8cm^{-1}). For the dispersed fluorescence spectrum exciting into the 99cm^{-1} (d_0^1) mode broadening occurred in the middle region making accurate assignments difficult. All the aforementioned

Figure 3.5 Energy level diagrams to illustrate two possible assignments of the first member transition in the fluorescence excitation spectrum of DMABN where:

- a) The 0_0^0 transition is absent.
- b) The first member is the origin transition.

a)



b)

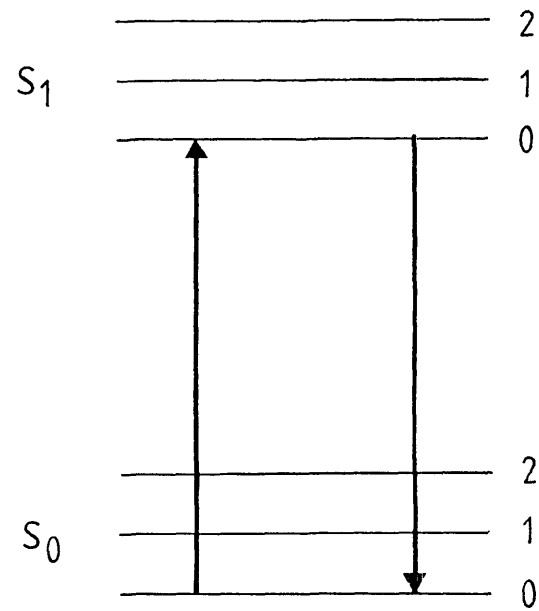


Table 3.3 Assignments of the 0_0^0 , 61 and **99** cm^{-1} fluorescence spectra of DMABN. Frequency values are accurate to $\pm 5\text{cm}^{-1}$.

0_0^0			61 cm^{-1} (c)			99 cm^{-1} (d)		
cm^{-1}	RI	Ass	cm^{-1}	RI	Ass	cm^{-1}	RI	Ass
0	100		0	100	c_0^1	0	100	d_0^1
72	24	b_1^0	76	68	$c_0^1 a_1^0$	65	28	$d_0^1 a_1^0$
115	16	c_1^0	121	32	c_1^1	112	48	$d_0^1 c_1^0$
136	68	d_1^0	157	8	$c_0^1 d_1^0$	153	72	$d_0^1 e_1^0$
194	48	e_1^0	202	20	$c_0^1 e_1^0$	194	12	$d_0^1 e_1^0$
230	20	f_1^0	228	12	$c_0^1 f_1^0$	257	52	
270	36		282	48		302	20	
311	28		353	44		354	48	
345	12		428	24	$c_0^1 6a_1^0$	452	20	broad ($d_0^1 6a_1^0 a_1^0$)
389	20		494	20	$c_0^1 6a_1^0 a_1^0$	484	20	
424	64	$6a_1^0$	560	24	$c_0^1 10b_2^0$	507	20	
492	44	$6a_1^0 a_1^0$	624	16	$c_0^1 10b_2^0 a_1^0$	528	28	
550	36	$10b_2^0$	695	20		796	52	$d_0^1 1_1^0$
581	20	$10b_2^0 a_1^0$	798	72	$c_0^1 1_1^0$	825	28	
627	24	$10b_2^0 c_1^0$	835	32		862	20	$d_0^1 1_1^0 a_1^0$
679	24		872	28	$c_0^1 1_1^0 a_1^0$	908	24	$d_0^1 1_1^0 c_1^0$
733	16		911	20	$c_1^1 1_1^0$	958	44	$d_1^1 1_1^0$
777	28		961	24	$c_0^1 1_1^0 d_1^0$			
806	12	1_1^0						
850	28							
882	16	$1_1^0 a_1^0$						
920	44	$1_1^0 c_1^0$						

RI = relative intensity
Ass = assignment

fundamental vibrations of benzene can then be resolved into the set spectral profile as shown for the excitation spectrum though with differing intensities. For the dispersed fluorescence spectra, in most cases, the relative intensities are also repeated. The transitions have been assigned as follows: 424cm^{-1} corresponds to the 6a mode, 550cm^{-1} to the 10b mode and 806cm^{-1} to the 1 mode vibrations of benzene. These ground state and excited state frequencies are listed in table 3.4 including those for the low frequency oscillations of DMABN and assignments for those based on table 3.1.

For all the dispersed fluorescence spectra studied, a search was made as far as $12,000\text{cm}^{-1}$ to the red of the resonance transition in order to detect the presence of the broad shifted emission that is characteristic of the a^* state. No such emission was found.

3.3.3 Fluorescence decay lifetimes

The time resolved emission of the states were recorded at excess vibrational energies, $E_v = 0 - 898\text{cm}^{-1}$. The fluorescence decay lifetimes, τ_f , have been listed on figure 3.2. A typical experimental time-resolved decay curve is presented in figure 3.6. The time resolved fluorescence exhibits a single exponential decay over the total E_v range studied. Figure 3.7 shows a plot of τ_f versus E_v . It can be seen from the plot

Table 3.4 Ground and excited state assignments for DMABN

Mode		Frequency (cm ⁻¹)		Assignment
		ground state	excited state	
D	d	149	104	CH ₃ -antitrotation
E	e	197	121	?
F	f	229	166	strongly mixed mode containing, pyramid, twist, CH ₃ -rotation and ring deformation
6a		426	373	C-C-C in plane bending
10b		555	494	C-H out of plane bending
1		800	780	ring breathing

Figure 3.6 Fluorescence decay curve for the O_0^0 transition of DMABN.

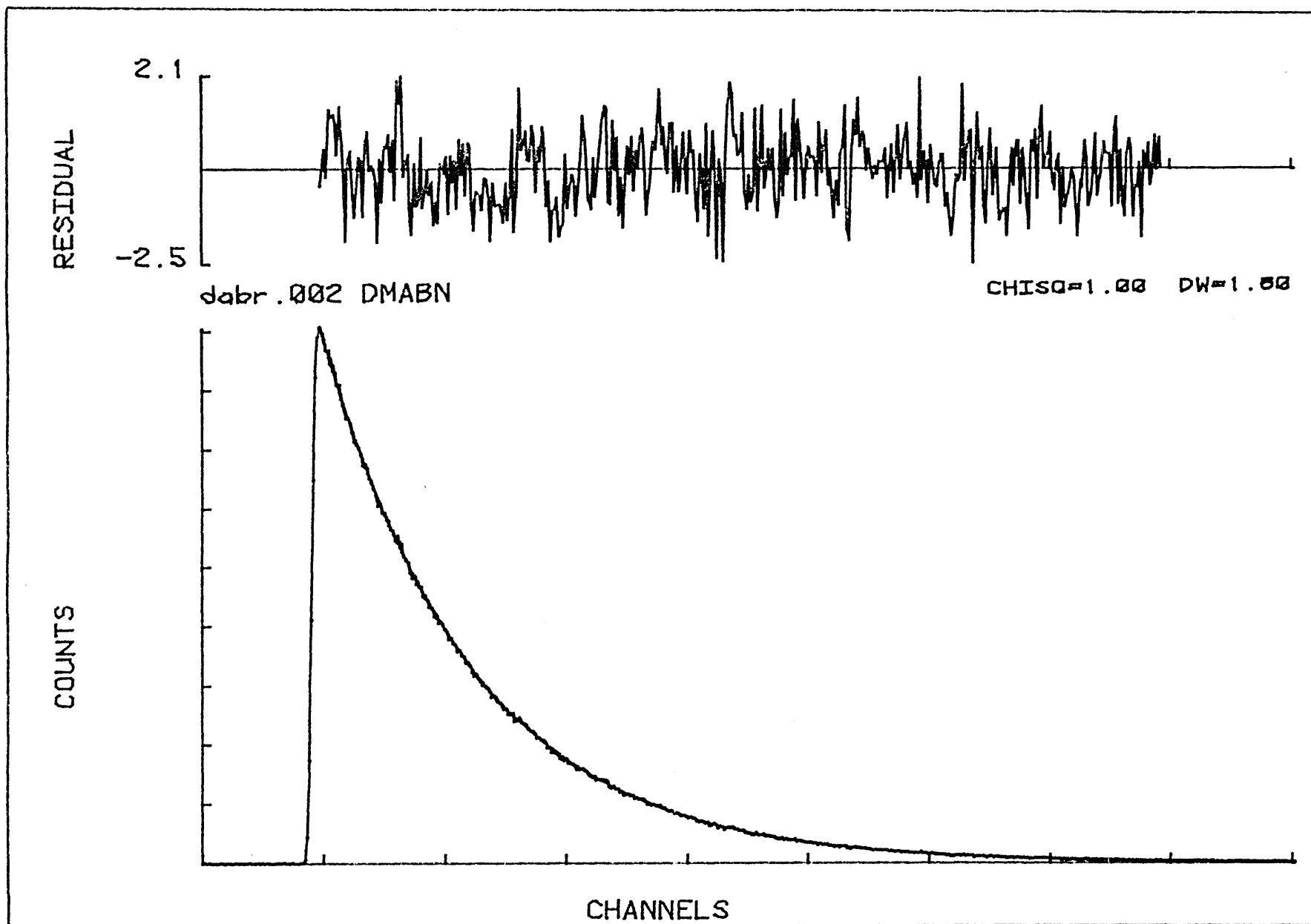
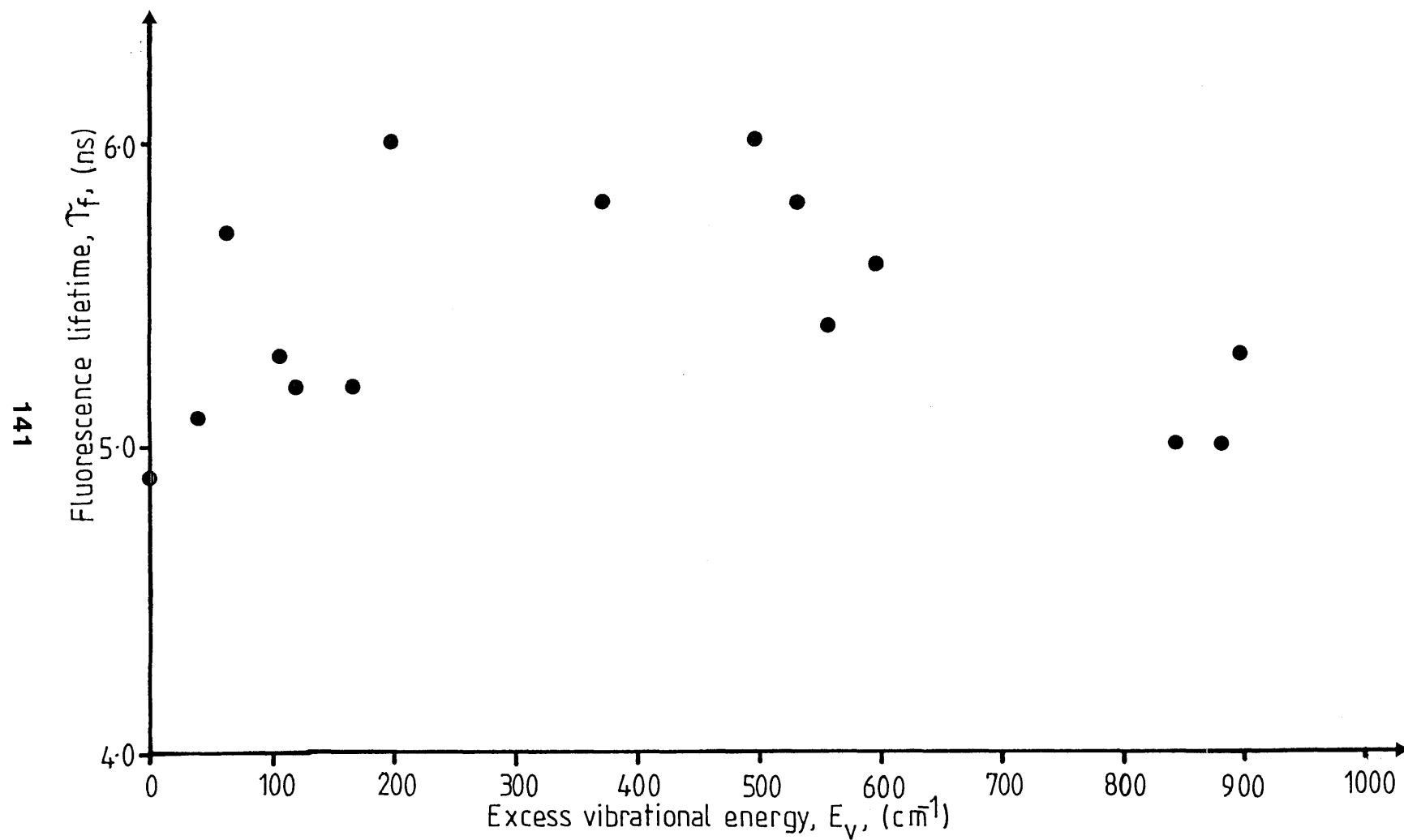


Figure 3.7 Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for selected excited vibronic levels of DMABN.



that initially there is an increase in τ_f in the low energy region $0 < E_v < 200\text{cm}^{-1}$, region A. From $200 < E_v < 898\text{cm}^{-1}$, region B, there is a weak dependence on excess vibrational energy which is shown as a small decrease in τ_f .

There is a certain deviation from A and B which cannot be attributed entirely to experimental error ($\pm 5\%$). It has been shown that the spectroscopy of DMABN is extremely complicated due to various oscillations of the amino group (see figure 3.1). The deviations from the general trends outlined above could possibly be due to measuring the τ_f of various combinations of the modes which would explain the reason for the scatter [20].

Another observation is that in figure 3.4a there is some unstructured emission in the 0_0^0 dispersed fluorescence spectrum. The ratio of unstructured/structured emission apparently decreases in the intense c_0^1 mode $\lambda_{\text{ex}} 61\text{cm}^{-1}$ and then increases for $\lambda_{\text{ex}} 99\text{cm}^{-1}$. The respective τ_f appear to follow this pattern also: 4.8: 5.7: 5.3ns.

3.3.4 DMABN-methanol complexes

The observation of the excitation spectrum of the DMABN-methanol complex was extremely dependent on the expansion conditions, in particular, the partial pressure of the methanol vapour. At low concentrations of methanol, new features appeared in the excitation

spectrum, as shown in figure 3.8, lying $18.9 \pm 5\text{cm}^{-1}$ to the blue of the bare molecule features. Increasing the partial pressure of methanol caused a decrease in the intensity of the bare molecule features and in the blue-shifted complex peak with the eventual disappearance of both. Complexes of higher stoichiometry were therefore being formed; however, no new excitation features due to these complexes could be formed, either to the higher or lower energy side of the bare molecule origin.

The dispersed fluorescence spectrum, following excitation of the 61cm^{-1} transition of the DMABN-methanol complex is shown in figure 3.9. The spectrum was recorded under low resolution conditions because of the low fluorescence quantum yield of the DMABN-methanol complex and so showed little well defined vibronic structure apart from the prominent feature at 800cm^{-1} . It closely resembles that of the bare molecule recorded under similar conditions. A search was made for the a^* emission from the complex but none was found.

The fluorescence lifetime of the DMABN-methanol complex was measured by exciting the 61cm^{-1} transition resulting in a mono-exponential decay with a lifetime of $5.2 \pm 0.5\text{ns}$.

3.3.5 DMABN-higher alcohol complexes

The formation of complexes of DMABN with ethanol, propan-1-ol and butan-1-ol were also

Figure 3.8 Fluorescence excitation spectrum of the DMABN-methanol complex. Complex features are indicated ($\downarrow$) relative to the corresponding bare molecule features, dashed lines indicate the position of complex peaks which are concealed by bare molecule peaks.

a) The origin region.

b) The 850 cm^{-1} region.

144

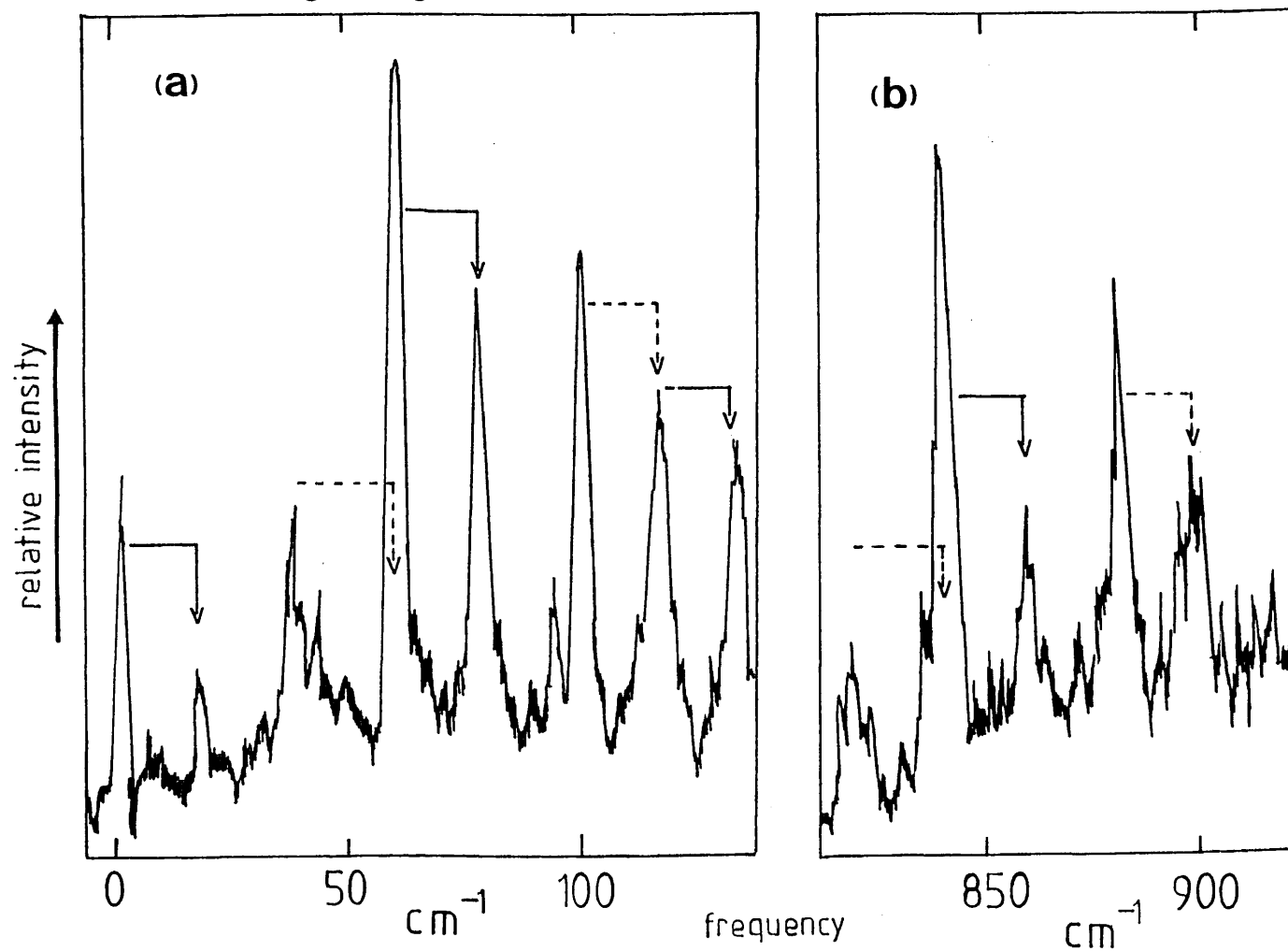
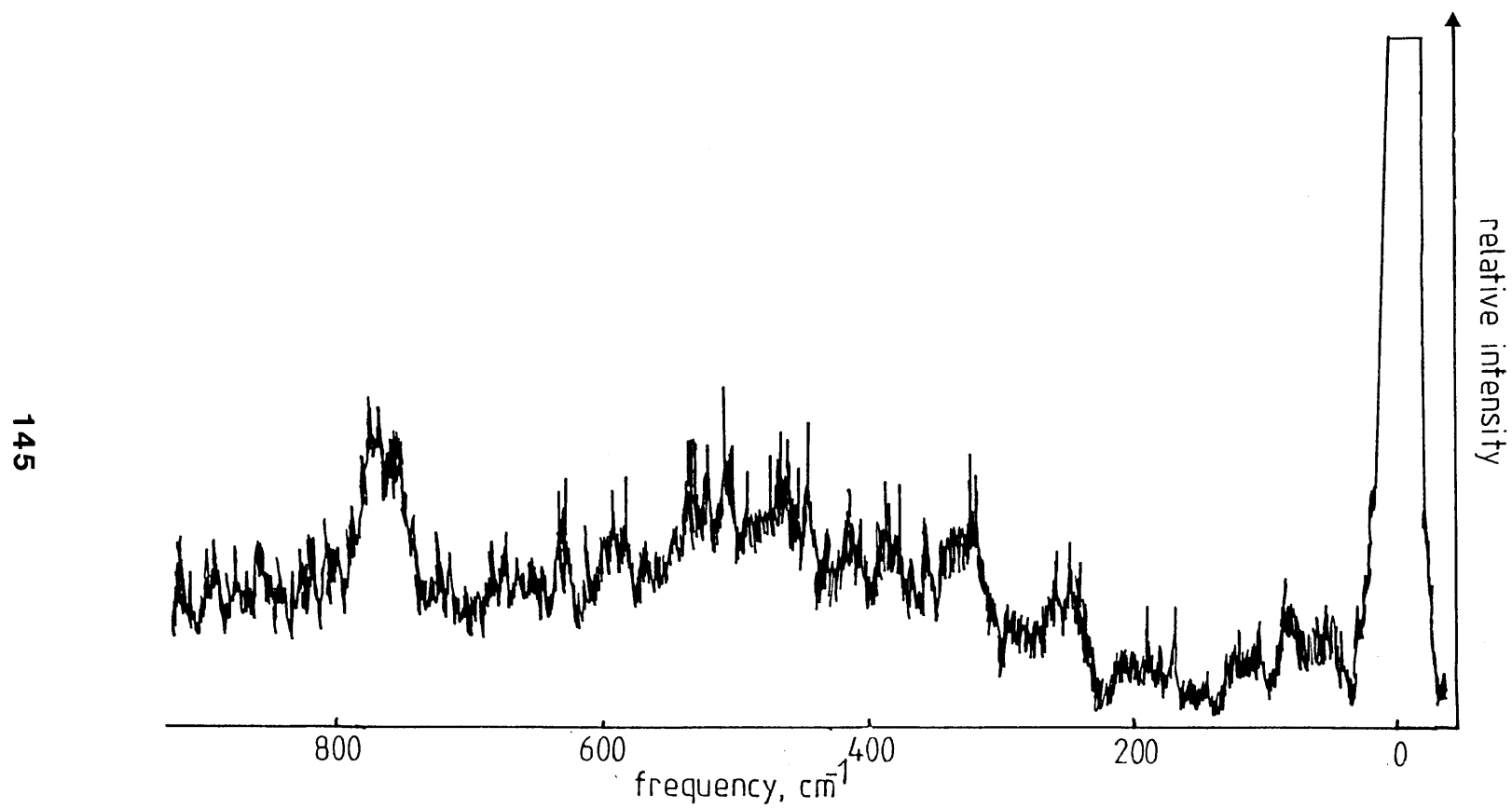


Figure 3.9 Dispersed fluorescence spectrum of the DMABN-methanol complex following excitation of the 61 cm^{-1} transition.



investigated over a wide range of solvent partial pressures (<1% to 100% of the carrier gas flow passing through the solvent reservoir). Over the entire range of partial pressures ethanol and butan-1-ol effectively quenched the bare molecule fluorescence but no excitation features due to complexes could be found. Introducing propan-1-ol into the expansion had little effect on the intensity of the bare molecule spectral features and complex formation seemed unfavourable under the expansion conditions used.

3.4 DISCUSSION

3.4.1 The bare molecule

According to the INDO calculations on DMABN [10] the most stable ground state structure in solution and in the gas phase is the planar geometry. The optically excited $^1B_2$ state also has planar geometry. The activity of low frequency, torsional modes in the DMABN excitation spectrum suggests, however, that the S_1 state may be twisted relative to the ground state. Rotkiewicz et al [21,22] have reported TICT state formation by 3,5-N,N-tetramethyl-4-aminobenzonitrile in the gas phase, that is, in the absence of solvent stabilisation. In the latter molecule, the dimethylamino group is forced into a twisted orientation as a result of steric hindrance by the ortho methyl groups. No such emission was detected for jet-cooled DMABN that could be

attributed to the TICT (a^*) state even when directly exciting torsional modes of the dimethylamino group. This suggests that either the amplitude of torsional oscillations excited (directly or as a result of vibrational redistribution) was insufficient or that solvent stabilisation is indeed necessary.

It has been assumed that the a^* state is emissive, however, this may not be the case under supersonic jet conditions, as discussed below. Even if the a^* state could not be detected by its fluorescence, its formation should still be manifested as the opening up of a non-radiative channel for the decay of the initially populated b^* state. The rise in background observed in the excitation spectrum in the middle region (figure 3.2b) is thought to be due to numerous unresolved combinations of low frequency oscillations of the amino group sitting upon the fundamental vibrations of benzene. These transitions are also found in N,N-dimethylaniline (see figure 3.3) and is not due to an emissive a^* state, a further indication being the lack of emission to the red of the dispersed fluorescence spectra and single exponential decay observed for all fluorescence lifetimes recorded, including those in the middle region.

3.4.2 Non-radiative decay channels

The essential invariance of the lifetime of DMABN across the excitation spectrum indicates that

radiationless decay be it intersystem crossing, internal conversion or a* state formation is not facilitated by vibrational excitation. Solution phase measurements indicate that intersystem crossing is the dominant non-radiative decay path for the b* state. Rettig et al [23] report a b* fluorescence lifetime of 6.2ns in n-butyl chloride/2-methylbutane at 77K, with a fluorescence quantum yield of 0.33 and a phosphorescence quantum yield of 0.66. The similarity of the above lifetime value and the present results suggests that intersystem crossing is the major decay channel in the jet-cooled molecule.

However, the threshold measurements for the onset of intramolecular vibrational distribution (IVR) generally rely on the appearance of unstructured emission as the indicator of IVR when the excitation wavelength is tuned to successively higher vibrational energies in the S₁ region. Fluorescence congestion is a sensitive marker and the appearance of congestion greater than expected from inhomogeneous broadening is a positive indication of extensive level mixing that is a prerequisite for IVR [24]. In longer chain alkyl benzenes [25] and in phenoxy alkanes [26] the onset for IVR is gauged by a broad red-shifted background in the single vibronic level fluorescence spectrum. It occurs relatively early on where E_v ~530cm⁻¹ [27].

In DMABN at λ_{ex} 840cm⁻¹ the fluorescence spectrum gave extremely broad unstructured fluorescence.

The evidence of unstructured fluorescence as shown in figure 3.4 suggests that IVR is occurring extremely early on.

3.4.3 DMABN-alcohol complexes

The dipole moment of the S_1 ($^1B_2$) state has been calculated to be almost 3 Debyes greater than that of the ground state [8]; therefore the observed blue spectral shift on methanol complexation is somewhat surprising. However, the behaviour is consistent with the recently reported results of Kobayashi et al [5] (and with results reported for 4-aminobenzonitrile complexes in Chapter 4) for DMABN complexes with H_2O and CF_3H and can be interpreted similarly. Because the spectral pattern of the low frequency transitions in the origin region reveals no significant change, apart from quenching of the fluorescence upon complexation, it can be said that the solvent molecule hardly affects the internal rotation of the dimethyl-amino moiety (figure 3.8). This suggests that the solvent molecule is interacting with the cyano group rather than the dimethylamino group and is thus having no effect on the low frequency oscillations. This argument is supported by:

(1) Solution phase results where the extent of solvatochromism is said to be less in dialkylamino substituted aromatics despite having a large electron donating capacity than the amino counterparts, the

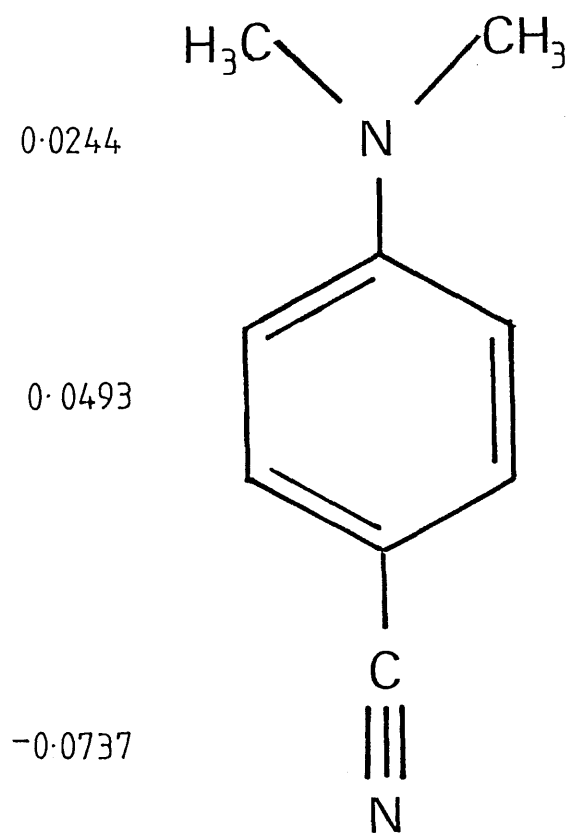
deviation being ascribed to methylamino group rotation [9] and to molecular size [28]

(2) Calculations of Lipinski et al [10], which show that the dipolar charge distribution of the ground state is largely associated with the benzonitrile moiety and that excitation to the $^1B_2$ state (short axis polarised) results in a reversal of the local benzonitrile dipole as a result of charge transfer from the dimethylamino group to the benzene ring as shown in figure 3.10. This is consistent with the observed decrease in binding energy of the complexes in the excited state. Solvent interaction of this type will not stabilise type a^* state and so it is not surprising that charge transfer fluorescence was not observed and the fluorescence lifetime of the complex was, within experimental error, equivalent to that of the bare molecule.

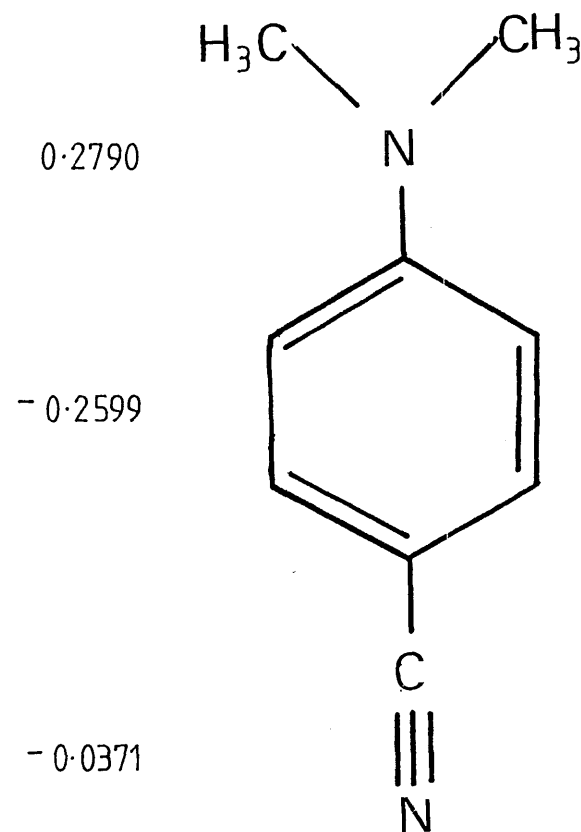
The solution phase experiments of Wang and Eisenthal [4] provide evidence that TICT (a^*) state formation is facilitated by the formation of ground state butan-1-ol complexes. In the supersonic jet, formation of the 1:1 complex between DMABN and methanol clearly does not provide the desired stabilisation. Complexes of higher stoichiometry, in which the solvent interacts with the dimethylamino group are expected to be precursors of the a^* state. No difficulty was found in forming such complexes between DMABN and methanol to the exclusion of the free molecule and the 1:1 complex, but their

Figure 3.10 Charge distribution in the ground state and in the lowest electronic states for DMABN.

a) ground state ($^1A_1$)



b) excited state ($^1B_2$)



excitation spectra could not be observed (with ethanol and butan-1-ol, no 1:1 complexes were observed, only 1:n ($n > 1$) complexes appeared to be formed). The formation of such complexes thus appears to result in a dramatic reduction in fluorescence quantum yield rather than the appearance of a^{*} emission.

Solution phase studies have shown that the quantum yield of TICT (a^{*}) fluorescence is an order of magnitude less than that of the unquenched b^{*} fluorescence. The lack of overlap between donor and acceptor orbitals in the twisted charge transfer state greatly diminishes the radiative decay rate and radiationless channels are expected to dominate. The zero point level of the solvated a^{*} state lies approximately 5,000cm⁻¹ below the initially excited ¹B₂ state [8]. In solution this excess energy is rapidly dissipated and emission is observed from low in the a^{*} manifold. In the supersonic jet, such vibrational relaxation cannot occur; internal conversion to the a^{*} state will leave the DMABN-alcohol complex in possession of some 5,000cm⁻¹ excess vibrational energy. The rate of non-radiative decay of such a high vibronic state, not least as a result of predissociation of the complex, is expected to be rapid. Thus, although there is no direct evidence of the a^{*} state, the behaviour of DMABN-solvent complexes is consistent with the formation of such a state which is non-emissive under supersonic jet

conditions.

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CHAPTER 4

SPECTROSCOPY OF 4-AMINOBENZONITRILE AND ITS VAN DER WAALS COMPLEXES

CHAPTER 4

SPECTROSCOPY OF 4-AMINOBENZONITRILE AND ITS VAN DER WAALS COMPLEXES

4.1 INTRODUCTION

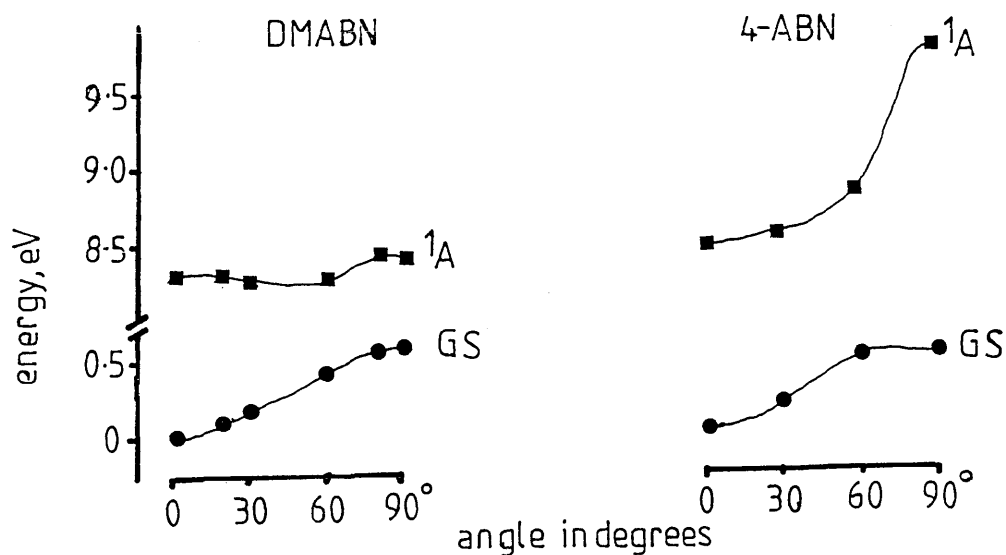
To aid the understanding of the behaviour of DMABN in the jet, the related but simplified system, 4-ABN, has been studied. Both molecules are members of a class of para di-substituted benzenes in which one substituent is an electron donor, D, and the other an electron acceptor, A: D-Ph-A [1]. The anomalous fluorescence of DMABN, which is attributed to the TICT state stabilised by polar solvation [2], has already been discussed in Chapter 1. Such behaviour is not expected for 4-ABN (nor observed) as explained below.

4.1.1 Absence of TICT emission in 4-ABN

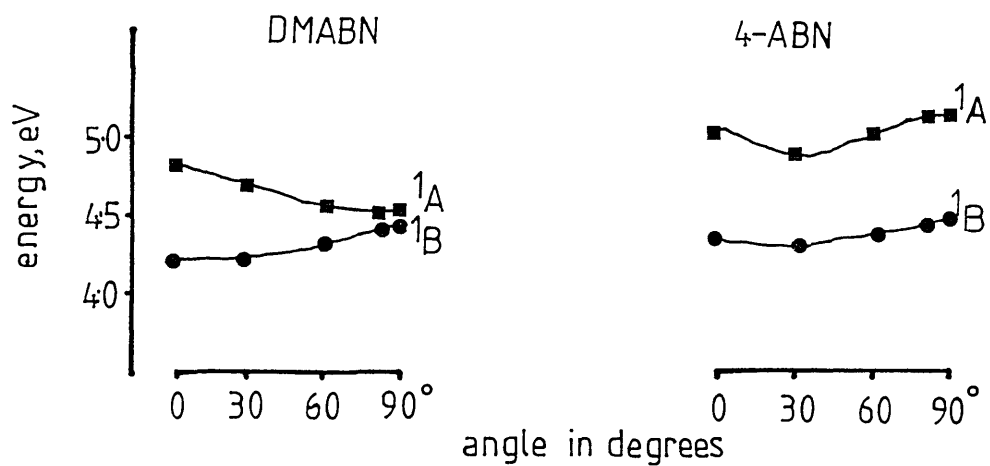
Rettig and Bonacic-Koutecky [3] carried out ab initio and CNDO/S calculations to support a mechanism involving geometrical relaxation of the amino group for the appearance of the a^* state in DMABN. The calculations were carried out on related compounds, including 4-ABN, and studied the influence of geometrical relaxation on the energy of the ^1A excited states of DMABN and 4-ABN. The a^* energy dependence on the rotation around the C-N bond shows a large difference between DMABN and 4-ABN as shown in figure 4.1a. In contrast to DMABN the energy difference between the

Figure 4.1 Theoretical calculations for ground and excited states of 4-ABN and DMABN.

a) Ab initio ground state GS(—●—) and singlet excited state ^1A (—■—) energies.



b) CNDO/S singlet excited state ^1B (—●—) and ^1A (—■—) energies.



triplet state and the ^1A state is large for the 90° twisted geometry of 4-ABN because the large charge separation in the singlet excited state, $^1A_1$, does not take place. The CNDO/S calculations reveal that for 4-ABN the energy difference

$$\Delta E = E(^1A) - E(^1B) \quad (1)$$

is larger in comparison with DMABN as well as for twisted geometries, mainly because the geometrical changes are not so favourable for the ^1A excited state (see figure 4.1(b)). The observed lack of the long wavelength fluorescence in 4-ABN was rationalised as being due to the less favourable energy behaviour of the ^1A excited state for the twisted geometries, the less polarised nature of this state and a larger energy difference, ΔE , in comparison with DMABN (figure 4.1). Hence, the unalkylated amino-group is an insufficiently strong electron donor to favour formation of a TICT state [3].

The fluorescence excitation spectrum of DMABN (Chapter 3) is complicated by low frequency progressions in a torsional mode of the dimethylamino group. In contrast, the spectrum of 4-ABN is not complicated by these low frequency transitions and can be assigned easily. Spectroscopically, 4-ABN closely resembles aniline rather than benzonitrile, and the amino inversion mode, which is described below, is active in both

excitation and dispersed fluorescence spectra.

4.1.2 Inversion vibration of the amino group

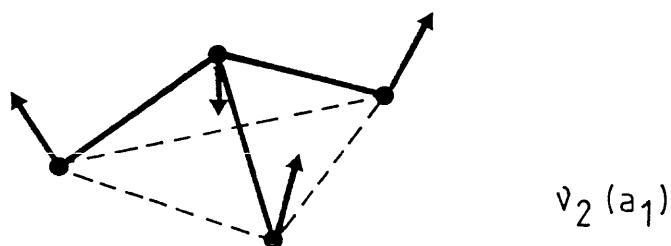
Because this vibration plays an important part in the spectroscopy of 4-ABN, an introduction will be given to the behaviour of the inversion mode found in ammonia and aniline to which 4-ABN behaves similarly.

The inversion vibration of ammonia, ν_2 , is illustrated in figure 4.2a. It has the symmetry species a_1 in the C_{3v} point group. The equilibrium configuration of NH_3 is pyramidal with $\angle HNH = 106.7^\circ$ but, for large amplitude motion in the vibrational mode, the molecule may go through the planar configuration to the pyramidal one which is identical to the first except that it is inverted. The planar and two equivalent vibrations are shown in figure 4.2b. The two pyramidal configurations correspond to identical minima in the potential energy curve and the planar form to an energy maximum. The energy difference, V_1 , between the minima and the maximum is the energy barrier and is the classical energy which is required to invert the pyramid.

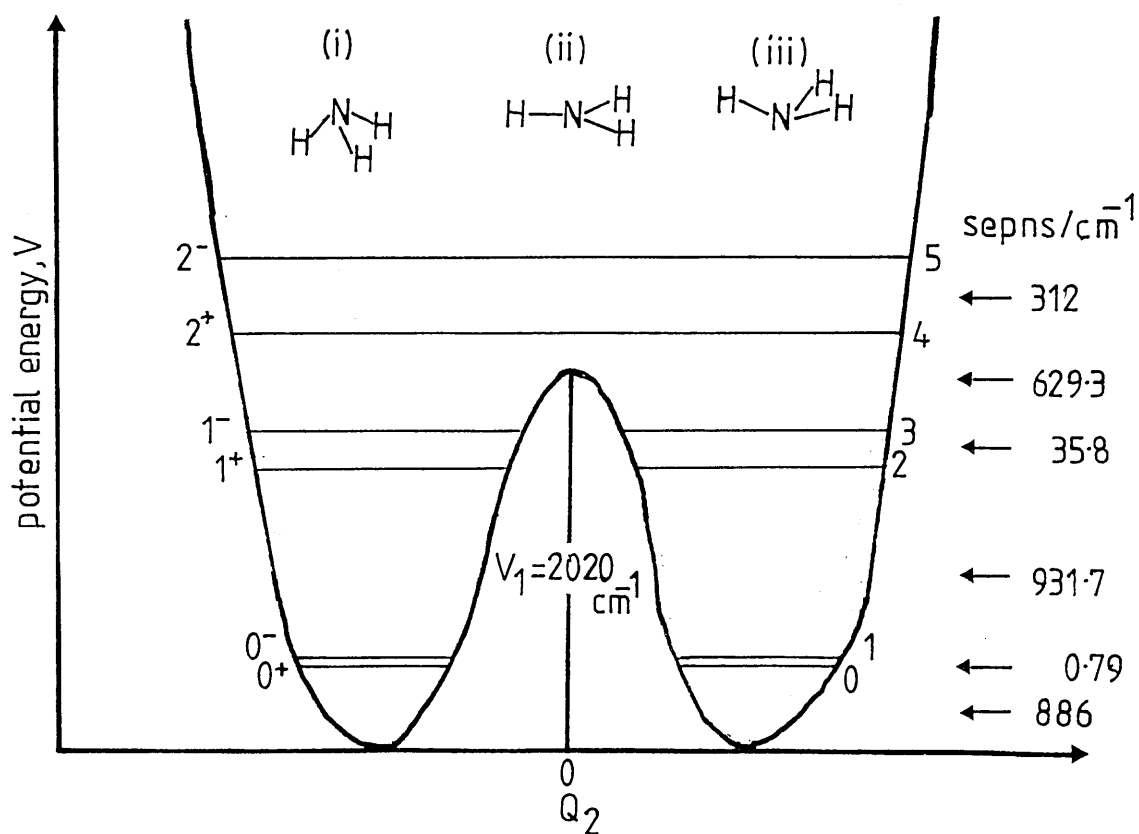
In a quantum mechanical system it may not be necessary to surmount the barrier in order to go from one equilibrium configuration to an equivalent one. The phenomenon of quantum mechanical tunnelling allows a degree of penetration of the barrier. If the barrier is sufficiently low or narrow (or both) the penetration may

Figure 4.2 a) Inversion vibration, ν_2 , of the NH_3 molecule.
b) Potential energy curve for ν_2 of the NH_3 molecule.

a)



b)

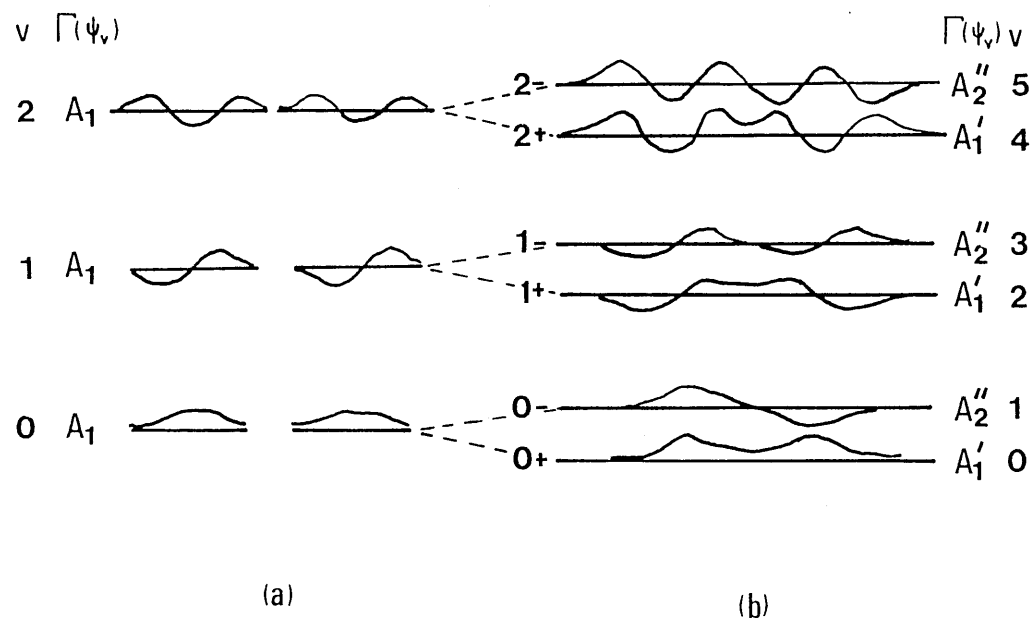


be so great that interaction may occur between the identical sets of vibrational levels in the two limbs of the potential energy curve. This interaction splits the levels into two components. The splitting becomes greater towards the top of the barrier where tunnelling is more effective.

The effect of tunnelling on the vibrational wave functions is shown in figure 4.3. The wave functions in figure 4.3a represent those for a potential function with an infinite barrier. Because there is no overlap, the energy when the two wavefunctions for each pair of vibrational levels is in-phase or out-of-phase, is unaffected.

As the barrier decreases (the case in figure 4.2) the wave functions for each vibrational level starts to overlap. Where this occurs the relative signs of the overlapping wavefunctions becomes important: they overlap either with the signs in-phase, as in the 0^+ , 1^+ , 2^+ , ... levels, or out-of-phase, as in the 0^- , 1^- , 2^- , ... levels. It can be seen (figure 4.3b) that all the wave functions arising from the out-of-phase combinations have a node, where $\psi_v = 0$, at the centre whereas the others have not. The fact that all the out-of-phase combinations result in an energy higher than that of the corresponding in-phase combinations follows from the general rule that additional nodes increase in energy [4].

Figure 4.3 The form of the vibrational wave function for an inversion vibration.



The barrier to planarity is (a) infinite and (b) moderately low

The labelling of the vibrational levels on the left-hand side of figure 4.3 uses the superscript + or - to indicate in-phase or out-of-phase combinations respectively. The wave functions ψ_v^+ and ψ_v^- corresponding to these levels are given by:

$$\begin{aligned}\psi_v^+ &= \psi_v(Q_2) + \psi_v(-Q_2) \\ \psi_v^- &= \psi_v(Q_2) - \psi_v(-Q_2)\end{aligned}\tag{2}$$

Where $Q_2 = 0$ corresponds to the planar configuration. The vibrational quantum number used in the label is that which is appropriate to the infinite barrier limit. On the right-hand side the labelling used is the vibrational quantum number appropriate to the zero barrier limit.

The rate of tunnelling through the barrier, that is, the rate at which the molecule inverts from one form to another, is directly related to the frequency separation $\Delta\nu$ of the vibrational levels in which the molecule finds itself. The time, τ , for inversion is given by:

$$\tau = (2 \Delta\nu)^{-1}\tag{3}$$

For ammonia the $\nu_2 = 0$ to $\nu_2 = 1$ (that is 0^- to 0^+) the separation is 23.786GHz [3]. From (3) it follows that time, τ , for inversion is 2.1×10^{-11} s.

There have been several suggested potential

functions which reproduce the double minimum potential shown in figure 4.2b. The most representative being proposed by Swalen and Ibers [5]:

$$V(Q) = 0.5aQ^2 + b\exp(-cQ^2) \quad (4)$$

Where a parabolic potential (first term) is perturbed by a gaussian barrier (second term). In ammonia the height of the barrier V_1 is 2022cm^{-1} , in aniline which exhibits the same behaviour the barrier is 450cm^{-1} .

In aniline, the hydrogen atoms of the NH_2 group are not coplanar with the rest of the molecule. The angle between the bisector of HNH and the plane of the rest of the molecule is 39.4° [4], as determined by microwave spectroscopy. Figure 4.2 illustrates that tunnelling through the barrier effectively introduces a plane of symmetry at $Q_2 = 0$ and the + or - wave functions are symmetric or antisymmetric respectively to reflection in this plane. The point group to which rigid aniline belongs is C_s , that is, only one element of point symmetry: a plane perpendicular to the ring plane. On taking the non-rigidity of the amino group into account a point group of higher order is required. In aniline the point group C_{2v} is used [6]. The same reasoning is applied to 4-ABN which is also assigned a C_{2v} point group.

The resulting pattern of vibrational levels for

ν_1 , the NH_2 -inversion in the S_0 and S_1 states of aniline, is shown in figure 4.4. The observed I_0^1 and I_0^2 sequence bands, as well as bands with $\Delta\nu_1 = 2$, are indicated in the figure. Single quantum transitions in this out-of-plane mode are forbidden by electronic dipole selection rules.

4.1.3 B-type double-headed rotational contours

4-ABN exhibits the same double-headed B-type rotational contours as found in aniline [7] and benzonitrile [8]. Each molecule has a characteristic momental ellipsoid which has the property that the distance between any point on the surface and the centre of mass is $1/I^{0.5}$, where I is the moment of inertia. In figure 4.5 the principle inertial axis of 4-ABN are shown. By convention $I_a < I_b < I_c$ and the corresponding axis to these principal moments of inertia are labelled a, b, and c. In 4-ABN, as in aniline, the moments of inertia are as defined in figure 4.5. $I_a < I_b \approx I_c$ and is known as a prolate asymmetric rotor [7,9].

Rotational line structure can be observed in electronic spectroscopy but under the spectral resolution of the laser used in the present work the individual bands are not observed. The rotational term values of an asymmetric rotor cannot be expressed as simple close formula as done with symmetric rotors [4]. The same rotational selection rules apply to electronic and

Figure 4.4 Vibronic transitions involving the NH_2 -inversion vibration in the $\tilde{A}^1\text{B}_2$ -- $\tilde{X}^1\text{A}_1$ system of the aniline molecule.

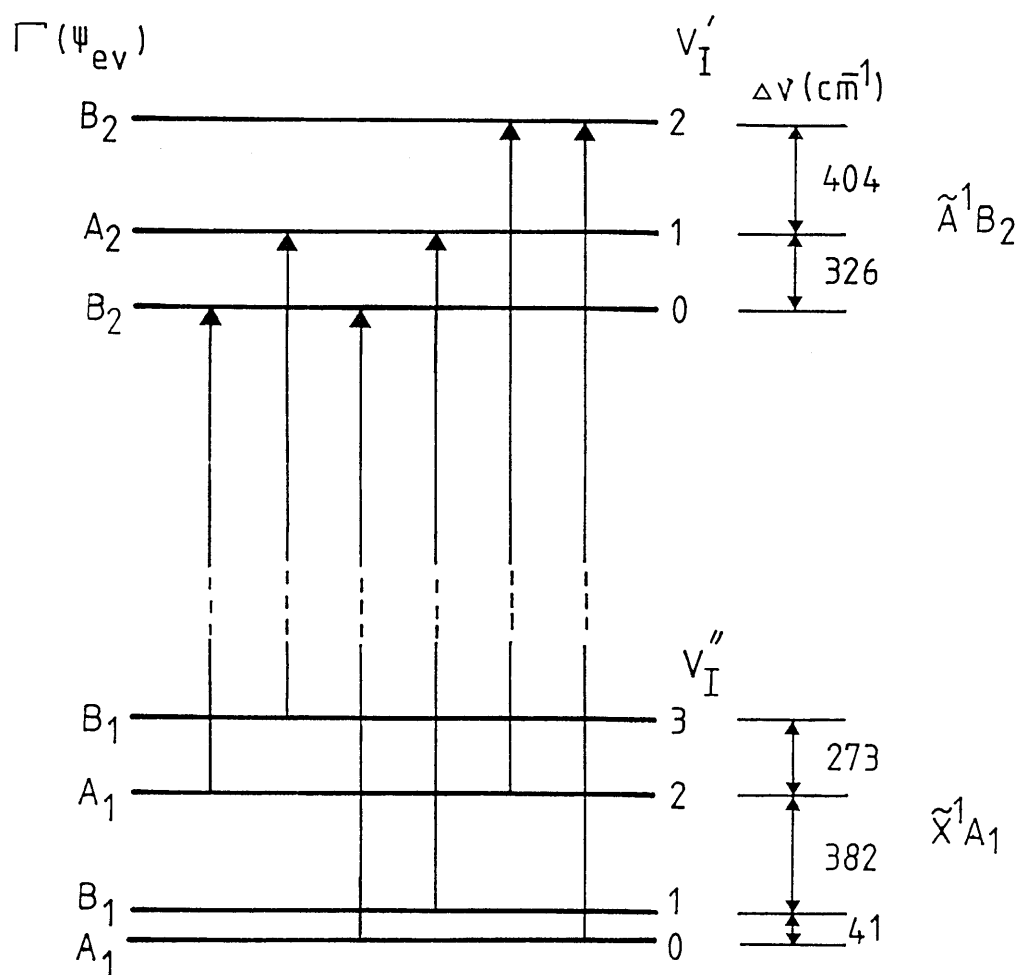
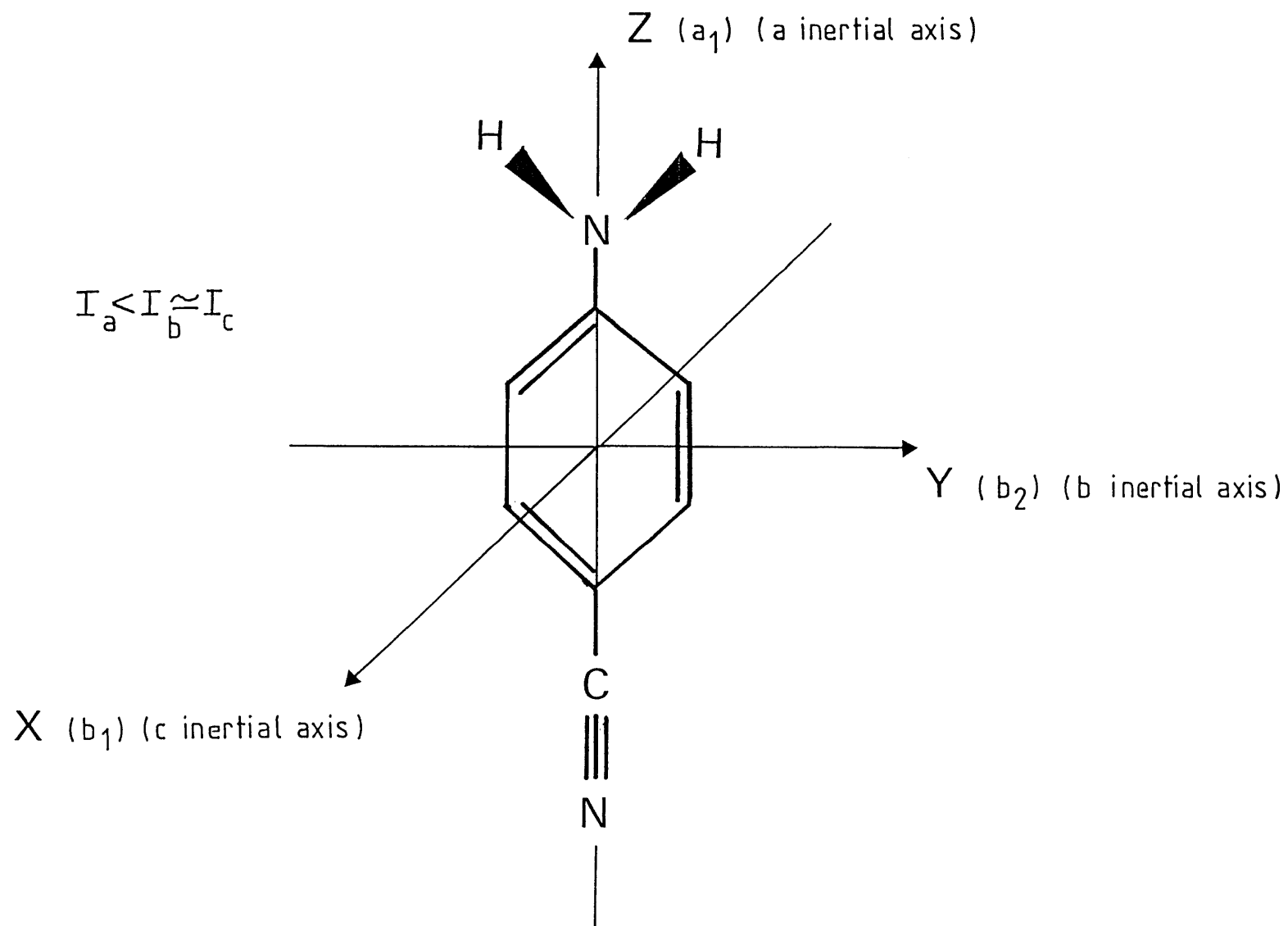


Figure 4.5 Transition dipole axes and inertial axis of 4-ABN.



vibronic electric dipole transitions between singlet states of asymmetric rotors as to infrared vibronic transitions. As a consequence type A, type B, type C or hybrid bands may result, depending on whether the oscillating electric dipole is set up along the a, b, c, inertial axis or between them. The difference between electronic and infrared (ir) vibrational transitions is that there is a larger change in rotational constant due to an electronic transition than a vibrational transition. Hence, the rotational contours are not typical A, B, or C bands as is in ir vibrational spectra. The bands are likely to be quite strongly degraded and degradation varies widely from one transition to another and from one molecule to another.

K corresponds to the asymmetry parameter for asymmetric rotors. The value of K used is -1 for a prolate asymmetric rotor and is written as K_{-1} or K_a and $+1$ for an oblate symmetric rotor, K_{+1} or K_c . Asymmetric rotors tend to behave like symmetric rotors for certain ranges of J (where J is the rotational quantum number) and K_a . A prolate asymmetric rotor tends to behave like an oblate symmetric rotor ($I_a = I_b < I_c$) for low K_a and high J . For high K_a and in particular when $J = K_a$ a prolate asymmetric rotor tends to behave like a prolate symmetric rotor. For these reasons it is usual for rotational fine structure of an asymmetric molecule to show regions of regularity.

In 4-ABN the transition of the 0_0^0 band, ${}^1B_2 \leftarrow {}^1A_1$, is polarised along the b axis and gives rise to a type B band [4,10] as found in aniline for which a double headed B-type band is observed [7,9]. The selection rules for a B-type band are

$$\begin{array}{ccc} K_a K_c & K_a K_c & \\ ee \longleftrightarrow & oo & \\ oe \longleftrightarrow & eo & \text{Where } e = \text{even, } o = \text{odd} \end{array}$$

as well as

$$\Delta J = 0, \pm 1$$

Benzonitrile also has C_{2v} symmetry. The band contour analysis of Brand and Knight [11] confirmed the electronic transition as also ${}^1B_2 \leftarrow {}^1A_1$. Thus the transition lies in the plane of the molecule (yz plane) along the y or b axis and perpendicular to the twofold (z) axis. Bands involving only totally symmetric vibrations are thus expected to be B-type. B-type bands have been shown by Brand and Knight to have double heads.

4.2 EXPERIMENTAL

4-ABN was obtained from Aldrich Ltd and used without further purification. The sample vapour (produced by heating the solid to 100°C) was mixed with helium carrier gas at a stagnation pressure of 3-4bar. The nozzle diameter was 87µm. The solvents used were of

a reagent grade and not purified further.

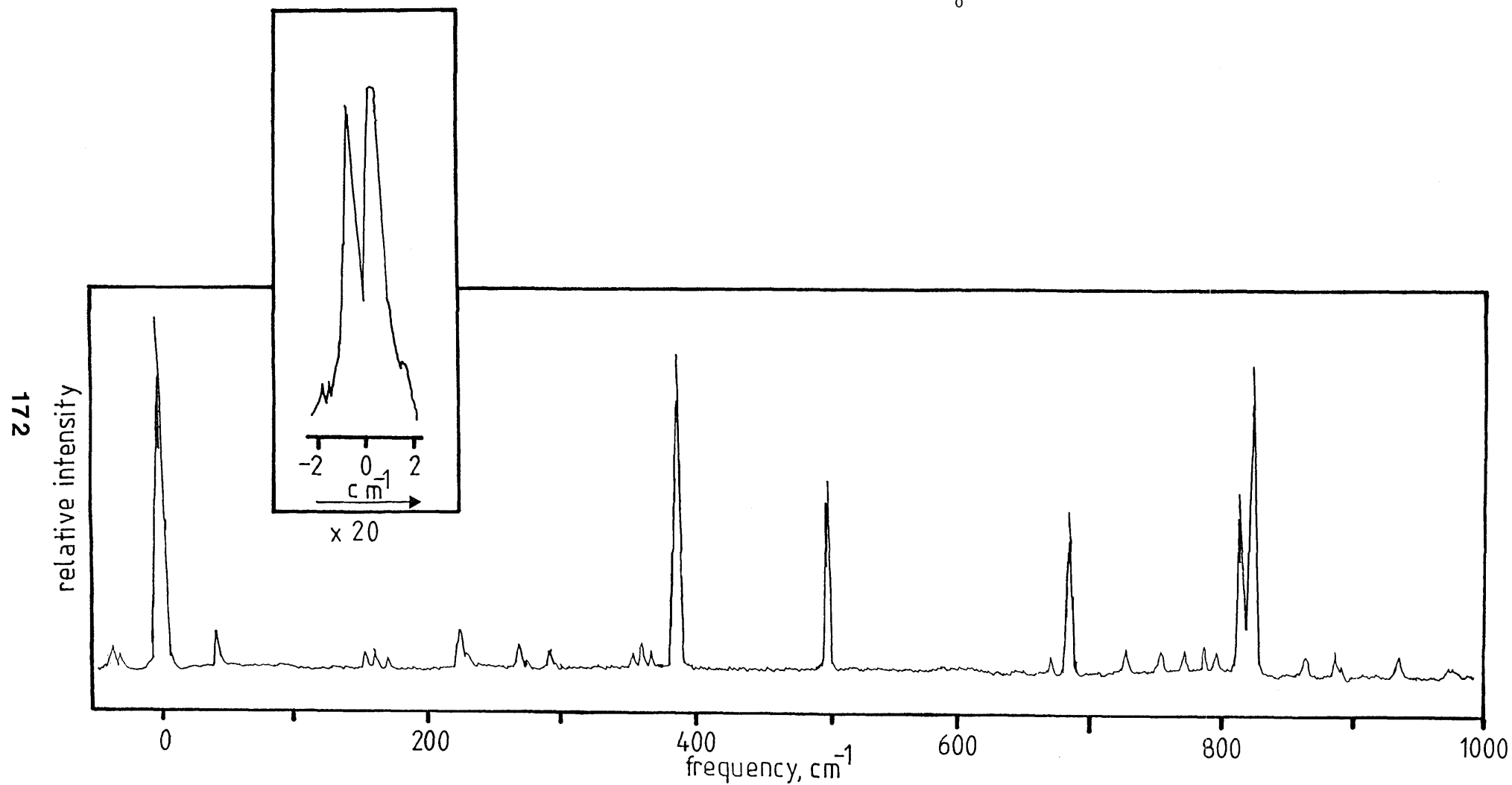
Quantum chemical calculations on the Hartee-Fock level were performed using the semi-empirical MNDO (Modified Neglect of Diatomic Differential Overlap) method to obtain optimised geometries of the bare molecules and 4-ABN water complexes. The MNDO-program is able to optimise automatically certain bond angles and distances as defined by the user. The calculations can give approximate qualitative indications of the structural forms of 4-ABN-complexes but are not intended to give reliable absolute energies and molecular geometries [12-14].

4.3 RESULTS AND DISCUSSION

4.3.1 The bare molecule

The fluorescence excitation spectrum of 4-ABN, shown in part in figure 4.6, displays an intense origin O_0^0 at 33493cm^{-1} and seven intense vibronic transitions in the first 1200cm^{-1} . Two sequence bands with approximately 5% of the origin intensity occur at -28 and -34cm^{-1} and may be assigned as 11_1^1 and 15_1^1 (in Varsanyi's notation, [15]) by analogy with the vapour phase absorption spectrum [16]. Modes $11(b_1)$ and $15(b_2)$ are the two lowest frequency normal modes with ground state frequencies of 120 and $\sim 170\text{cm}^{-1}$ respectively [16]. The characteristic pattern of low frequency transitions which

Figure 4.6 Fluorescence excitation spectrum of 4-ABN. The inset shows the rotational contour of the 0_0^0 transition.



dominates the spectrum of DMABN is absent from the 4-ABN spectrum. These low frequency transitions, which are also observed in the spectrum of jet-cooled N,N-dimethylaniline (DMA) (see Chapter 3), appear to be associated specifically with the N,N-dimethylamino group.

The $S_1 \leftarrow S_0$ transition in 4-ABN is ${}^1B_2 \leftarrow {}^1A_1$, short axis polarised. Since the approximate molecular symmetry of aniline in the ground state is C_{2v} and the inversion vibration is classified as a "non-totally symmetric" vibration of b_1 symmetry, any transition between vibronic states of different parity of the vibrational quanta in the ground and excited states is regarded as "forbidden" [17]. The same applies to 4-ABN. The use of the C_{2v} point group classification acknowledges the fact that although the inversion motion of the NH_2 group yields prominent features in the spectrum, no torsional splittings are seen [18].

The O_0^0 band exhibits a double headed, B-type, rotational contour (figure 4.6), similar to those observed in jet-cooled benzonitrile [8,19] and jet-cooled aniline [20]. All seven intense vibronic bands exhibit similar double headed structure and thus correspond to totally symmetric transitions. Four of these transitions can be assigned to fundamentals characteristic of substituted benzenes: 6a, 12, 1 and 13 (Varsanyi's notation, see Chapter 1 section 1.6 [15]) as listed in table 4.1. These transitions are prominent in

TABLE 4.1 Comparison of the frequencies of the optically active modes of 4-ABN with those of aniline, p-methylaniline and benzonitrile.

Mode ^a	4-ABN ^b		Aniline		p-methylaniline ^c		Benzonitrile	
	$\bar{\nu}'/\text{cm}^{-1}$	$\bar{\nu}''/\text{cm}^{-1}$	$\bar{\nu}'$	$\bar{\nu}''$	$\bar{\nu}'$	$\bar{\nu}''$	$\bar{\nu}'$	$\bar{\nu}''$
6a	382	412	491 ^c , 492 ^d	535 ^c	433	479	-	459 ^f
12	678	728	955 ^d	1013 ^c	-	-	703 ^e	769 ^f , 758 ^f
1	815	886	796 ^c , 798 ^d	824 ^c	817	851	946 ^e	1001 ^f
13	1164	1223	1311 ^d , 1307 ^g	1278 ^g	-	-	-	1192 ^f
l(v=2)	807	430	759 ^c , 761 ^d	427 ^c	737	443	-	-
l(v=4)	-	1365	1729 ^h	1089 ^h				

a Varsanyi notation for benzene derivatives [15]

b present work

c [22]

d [17]

e [21]

f [19]

g [18]

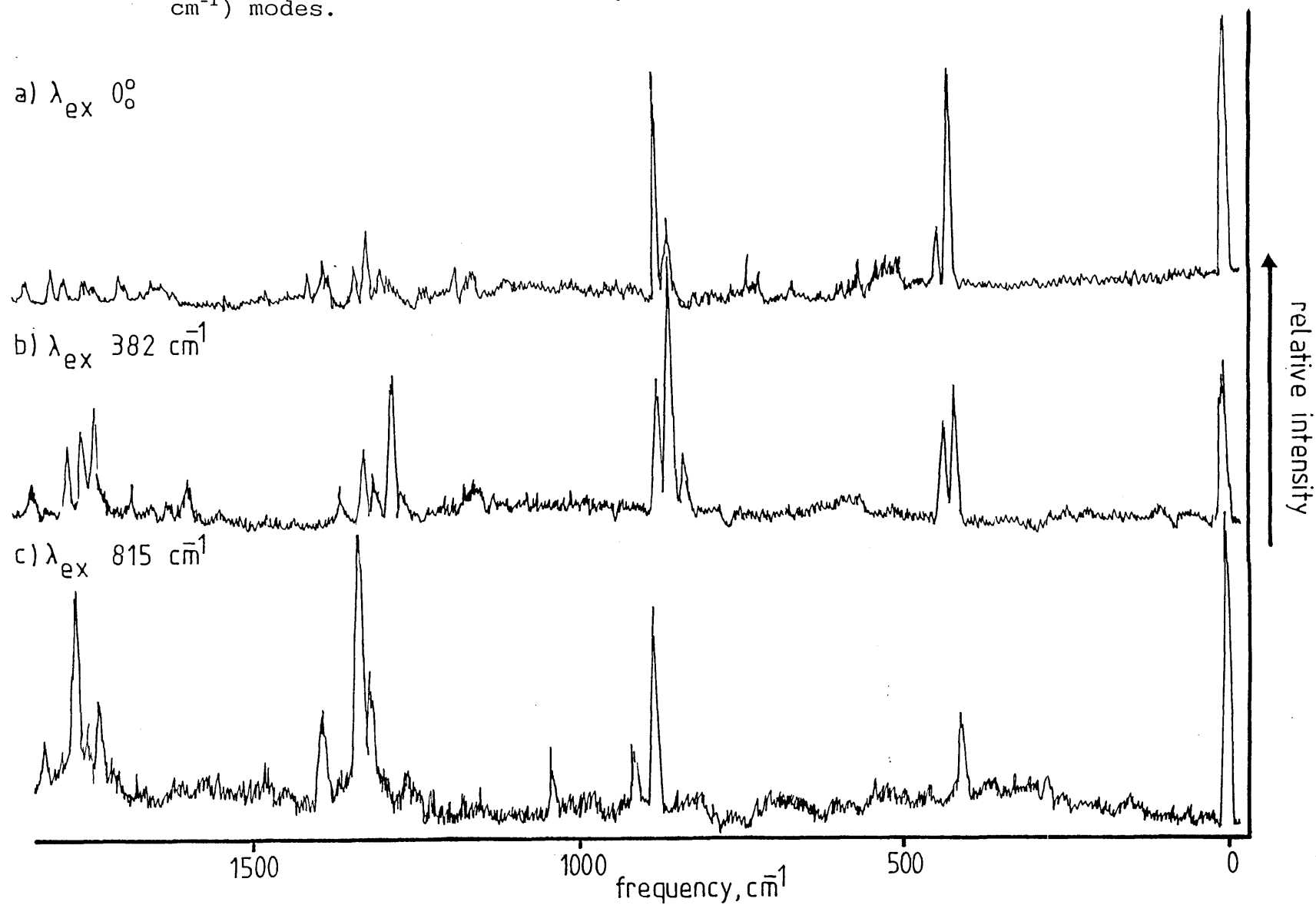
h calculated value [9]

the vapour phase absorption spectrum of 4-ABN reported by Ram et al [16]; however a considerable number of strong bands observed by Ram and assigned as transitions from $v'' = 0$ do not appear in the jet spectrum. The intense band at 1197cm^{-1} is assigned as the $1_0^1 6a_0^1$ combination. The two remaining intense transitions at 493 and 807cm^{-1} do not appear to correspond to a_1 fundamentals but to overtones of asymmetric vibrations, as discussed below.

In table 4.1, the frequencies of the four active fundamentals are compared with those observed for aniline, p-methylaniline and benzonitrile. The same four modes dominate the excitation spectrum of jet-cooled aniline [17], whereas only two of them, 12 and 1, are observed in the spectrum of jet-cooled benzonitrile [8].

The spectroscopic similarity between 4-ABN and aniline becomes more apparent in the dispersed fluorescence spectra. The fluorescence spectrum following 0_0^0 excitation is shown in figure 4.7. It deviates considerably from mirror symmetry with the excitation spectrum, the most notable difference being the appearance of a second band in the 400cm^{-1} region. This closely resembles the behaviour of aniline, where the strong anharmonicity of the inversion potential in the ground state leads to the appearance of the symmetry allowed I_2^0 transition at 427cm^{-1} in the fluorescence spectrum, whereas the I_0^2 transition occurs at 760cm^{-1} in excitation [8,22]. The band at 430cm^{-1} in the 4-ABN

Figure 4.7 Dispersed fluorescence excitation spectra of 4-ABN following excitation into a) 0_0^0 , b) $6a_0^1$ (382 cm^{-1}) and c) 1_0^1 (815 cm^{-1}) modes.



origin fluorescence spectrum is therefore assigned to the $\Delta v = 2$ transition in the amino group inversion mode. The 807cm^{-1} band in the excitation spectrum is in the right spectral region for I_0^2 transition and, as discussed below, the fluorescence spectrum from this level supports this assignment.

As can be seen from the assignments given in table 4.2, the origin fluorescence spectrum is dominated by the 6a mode, in progression and in combination with modes 1, 9a and 12 and with I_2 . Comparison with the assignment of the corresponding dispersed fluorescence of jet-cooled aniline [22] reveals a marked similarity in the fundamentals and combinations observed. Assignments of dispersed fluorescence spectra following excitation of the $6a_0^1$, 12_0^1 , 1_0^1 and 13_0^1 transitions are also given in table 4.2, revealing the ground state frequencies of these modes which are summarised in table 4.1. Transitions involving 6a and I_2 are prominent in all of the spectra. An unassigned frequency (labelled X) at $\sim 276\text{cm}^{-1}$ appears in combination with 6a and I_2^2 in the 0_0^0 excited spectrum and is particularly active in the 12_0^1 spectrum. No symmetric vibration of comparable frequency has been reported from infrared and Raman studies [11,23]; possible assignments for this transition are 11_1^0 , 15_1^0 or $11_1^0 15_1^0$.

Dispersed fluorescence spectra following excitation of the intense 493cm^{-1} and 807cm^{-1} transitions

TABLE 4-2

Assignments of dispersed fluorescence spectra of 4-ABN

0_0^0 excitation			$6a_0^1$ (382 cm^{-1}) excitation			12_0^1 (678 cm^{-1}) excitation			1_0^1 (815 cm^{-1}) excitation			13_0^1 (1164 cm^{-1}) excitation		
$\Delta\tilde{\nu}/\text{cm}^{-1}$	relative intensity	assignment	$\Delta\tilde{\nu}/\text{cm}^{-1}$	relative intensity	assignment	$\Delta\tilde{\nu}/\text{cm}^{-1}$	relative intensity	assignment	$\Delta\tilde{\nu}/\text{cm}^{-1}$	relative intensity	assignment	$\Delta\tilde{\nu}/\text{cm}^{-1}$	relative intensity	assignment
0	100	0_0^0	0	57	$6a_0^1$	0	65	12_0^1	0	87	1_0^1	0	100	13_0^1
412	79	$6a_0^0$	414	57	$6a_1^1$	411	21	$12_0^1 6a_0^0$	419	29	$1_0^1 6a_1^0 / 1_1^0 1_2^0$	417	26	$13_0^1 6a_1^0 / 13_0^1 1_2^0$
429	31	$1_2^0 1_2^0$	431	41	$6a_0^1 1_2^0$	691	47	$12_0^1 6a_0^0 X$	886	61	1_1^1	848	28	$13_0^1 6a_1^0 1_2^0$
688	10	$6a_0^0 X$	810	23	—	706	85	$12_0^1 1_2^0 X$	917	20	—	1009	20	—
705	18	$1_2^0 X$	826	100	$6a_2^1$	728	70	12_1^1	1039	20	$1_0^1 18a_1^0$	1076	24	—
823	33	$6a_2^0$	846	53	$6a_1^1 1_2^0$	1105	70	$12_0^1 6a_2^0 X$	1299	41	$1_1^1 6a_1^0$	1186	20	—
840	84	$6a_1^0 1_2^0$	1219	12	$6a_1^1 13_1^0$	1114	100	$12_0^1 6a_1^0 1_2^0 X$	1316	100	$1_1^1 1_2^0$	1223	70	13_1^1
1128	15	$6a_0^0 12_1^0$	1236	64	$6a_3^0$	1136	43	$12_1^1 6a_1^0$	1371	29	—	1261	22	$13_1^1 6a_2^0 1_2^0$
1230	10	$6a_3^0$	1257	18	$6a_2^1 1_2^0$	1150	28	—	1690	29	$1_0^1 6a_1^0 9a_1^0$	1316	26	$13_0^1 1_1^0 1_2^0$
1252	33	$6a_2^0 1_2^0$	1275	30	$6a_1^1 9a_0^0$	1174	38	—	1725	66	$1_1^1 6a_1^0 1_2^0$	1439	22	—
1271	15	$9a_0^0$	1308	15	$6a_1^1 1_1^0$	1255	47	$12_0^1 6a_2^0 1_2^0$	2077	21	$1_0^1 18a_2^0$	1489	20	—
1308	20	$1_1^0 6a_1^0$	1516	16	—	1400	32	$12_0^1 6a_1^0 1_2^0 X$	2103	25	$1_0^1 6a_2^0 9a_1^0$	1505	16	—
1315	33	$1_1^0 1_2^0$	1594	14	$6a_0^1 8a_1^0$	1430	36	$12_1^1 1_2^0 X$	2138	25	$1_1^1 6a_2^0 1_2^0$	1598	20	$13_0^1 8a_1^0$
1336	19	—	1648	41	$6a_4^1$	1527	64	$12_1^1 6a_2^0 X$				1631	39	$13_1^1 6a_1^0$
1593	19	$8a_1^0$	1665	35	$6a_3^1 1_2^0$	1546	70	$12_1^1 6a_2^0$				1690	22	$13_0^1 6a_1^0 9a_0^0$
1628	9	—	1683	27	$6a_1^1 9a_1^0$	1965	38	$12_1^1 6a_3^0$				1728	18	$13_0^1 1_1^0 6a_1^0 1_2^0$
1638	17	—	1731	15	$6a_1^1 1_1^0 1_2^0$	1982	53	$12_1^1 6a_2^0 1_2^0$						
1645	17	$6a_4^0$												
1669	17	$6a_3^0 1_2^0$												
1688	35	$6a_1^0 9a_1^0$												
1730	15	$1_1^0 6a_1^0 1_2^0$												

(which are not assignable to a_1 fundamentals) were also recorded (figure 4.8). The most intense fluorescence transition from the 493cm^{-1} level occurs at 552cm^{-1} . This is assumed to be the $\Delta v = 0$ transition and is assigned as $10b_2^2$ (and hence the 493cm^{-1} transition in absorption is assigned as $10b_0^2$). This gives a value of 276cm^{-1} for the ground state frequency of the $10b$ (b_1) mode in good agreement with the value of 280cm^{-1} from infrared absorption [24].

The fluorescence spectrum from the 807cm^{-1} level is anomalous in that the most intense transition occurs at 1365cm^{-1} . The large frequency change suggests that this is not a $\Delta v = 0$ transition; neither does it correspond to a $\Delta v = 2$ transition from the $v' = 2$ level of a harmonic asymmetric mode (such a transition would be expected to occur in the 1600cm^{-1} region). This spectrum is, however, consistent with the assignment of the 807cm^{-1} absorption as I_0^2 ; the intense 1365cm^{-1} fluorescence band can then be attributed to the I_4^2 transition. Assignments for the above two modes are given in table 4.3.

Because the planar form of the molecule can be stabilised through delocalization of the nitrogen lone pair into the π -system of the ring, one might expect a smaller angle of pyramidalization and a smaller barrier to nitrogen inversion in aniline than in aliphatic amines [25]. As discussed in section 4.1.2 in aniline, in

Figure 4.8 Dispersed fluorescence excitation spectra of 4-ABN following excitation into a) $10b_0^2$ (493 cm^{-1}) and b) I_0^2 (807 cm^{-1}).

180

a) $\lambda_{\text{ex}}\ 493\text{ cm}^{-1}$

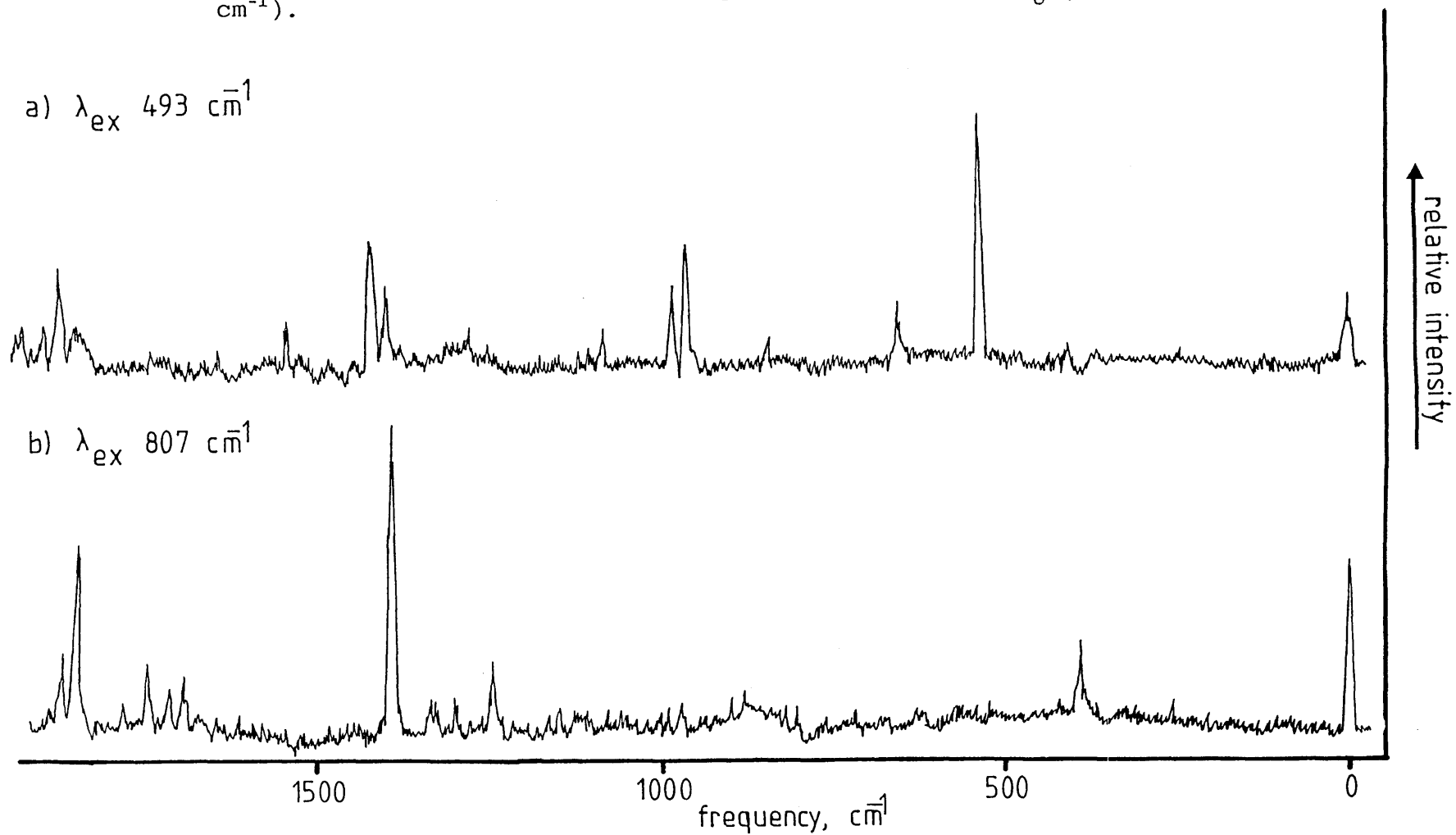


Table 4.3 Assignments of dispersed fluorescence spectra of 4-ABN, exciting into the $10b_0^2$ and I_0^2 modes.

$10b_0^2$ (493cm^{-1}) excitation			I_0^2 (807cm^{-1}) excitation		
$\Delta\nu/\text{cm}^{-1}$	RI	Ass	$\Delta\nu/\text{cm}^{-1}$	RI	Ass
0	26	$10b_0^2$	0	61	I_0^2
425	12	$10b_0^2 I_2^0$	416	25	$I_{06}^2 a_1^0$
554	100	$10b_2^2$	1231	23	I_{013}^2
667	29		1281	12	$I_{09}^2 a_1^0$
968	29	$10b_0^2 6a_1^0$	1316	13	I_{21}^2
988	53	$10b_0^2 I_1^0$	1365	100	I_4^2
1078	16	$10b_4^2$	1596	9	$I_{08}^2 a_1^0$
1377	33		1623	9	
1397	55	$10b_2^2 6a_1^0 I_2^0$	1643	19	$I_{06}^2 a_4^0$
1510	24	$10b_4^2 6a_1^0$	1662	14	$I_{46}^2 a_3^0$
1531	64	$10b_4^2 I_2^0$	1683	21	$I_{06}^2 a_1^0 9a_1^0$
1788	16		1707	9	$I_{29}^2 a_1^0$
1811	39	$10b_0^2 6a_2^0 I_2^0$	1784	58	$I_{46}^2 a_1^0$
1831	16		1802	26	
1862	16		2063	19	$I_{46}^2 a_1^0 X$
1889	16		2077	21	
2244	24		2097	9	
			2107	9	
			2194	28	$I_{46}^2 a_1^0$
			2216	79	

RI = Relative Intensity
Ass = Assignment

the ground state, the amino group is pyramidal [6,9,24, 26-28]: the angle θ , between the ring plane and the NH_2 plane is $\sim 39^\circ$ and the barrier to inversion is $\sim 450\text{cm}^{-1}$ [4]. In the S_1 state the barrier is greatly reduced; the potential is predicted to be essentially quartic with zero barrier [9]. Calculations were made of the ground state geometries of aniline and 4-ABN using the MNDO program described above, for which values of the out of plane angle, θ , of 23° for aniline and 19° for 4-ABN was obtained. Although substantially underestimating the out of plane angle, these results do indicate a similar degree of non-planarity in the two molecules.

4.3.2 4-ABN complexes

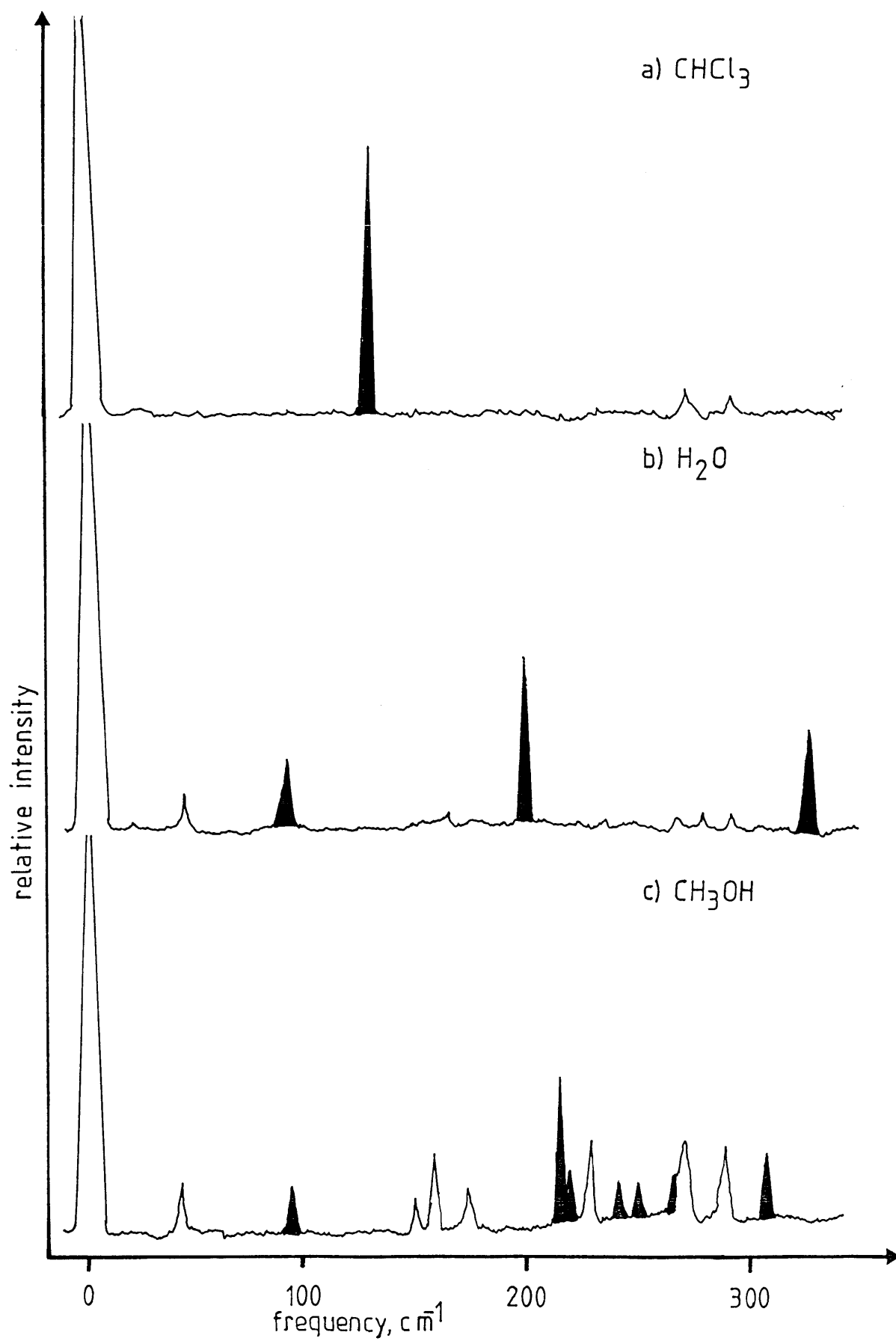
Complexes of 4-ABN with argon, alkylcyanides (RCN), water, chloroform and methanol have been investigated.

When 4-ABN was seeded in He containing a few percent of the solvent species several new bands appeared close to the vibronic bands of the monomer on the high energy side, with the exception of argon, as summarised in table 4.4 and as demonstrated by the complex features observed with chloroform, water and methanol in figure 4.9. The nature of the intermolecular interactions and the probable structures of these complexes are considered below. A qualitative interpretation of the observed rotational profiles of the complex excitation features is

Table 4.4 Microscopic solvent shifts exhibited by 4-ABN
van der Waals complexes.

Ligand	$\Delta\nu/\text{cm}^{-1}$
Ar	-47
Ar ₂	-93
CHCl ₃	128
CH ₃ CN	236
C ₂ H ₅ CN	239
i-C ₃ H ₇ CN	238
H ₂ O	84
	196
	314
CH ₃ OH	92
	210
	215
	239
	249
	305

Figure 4.9 Fluorescence excitation spectra of a) 4-ABN-CHCl₃, b) 4-ABN-H₂O and c) 4-ABN-CH₃OH complexes.



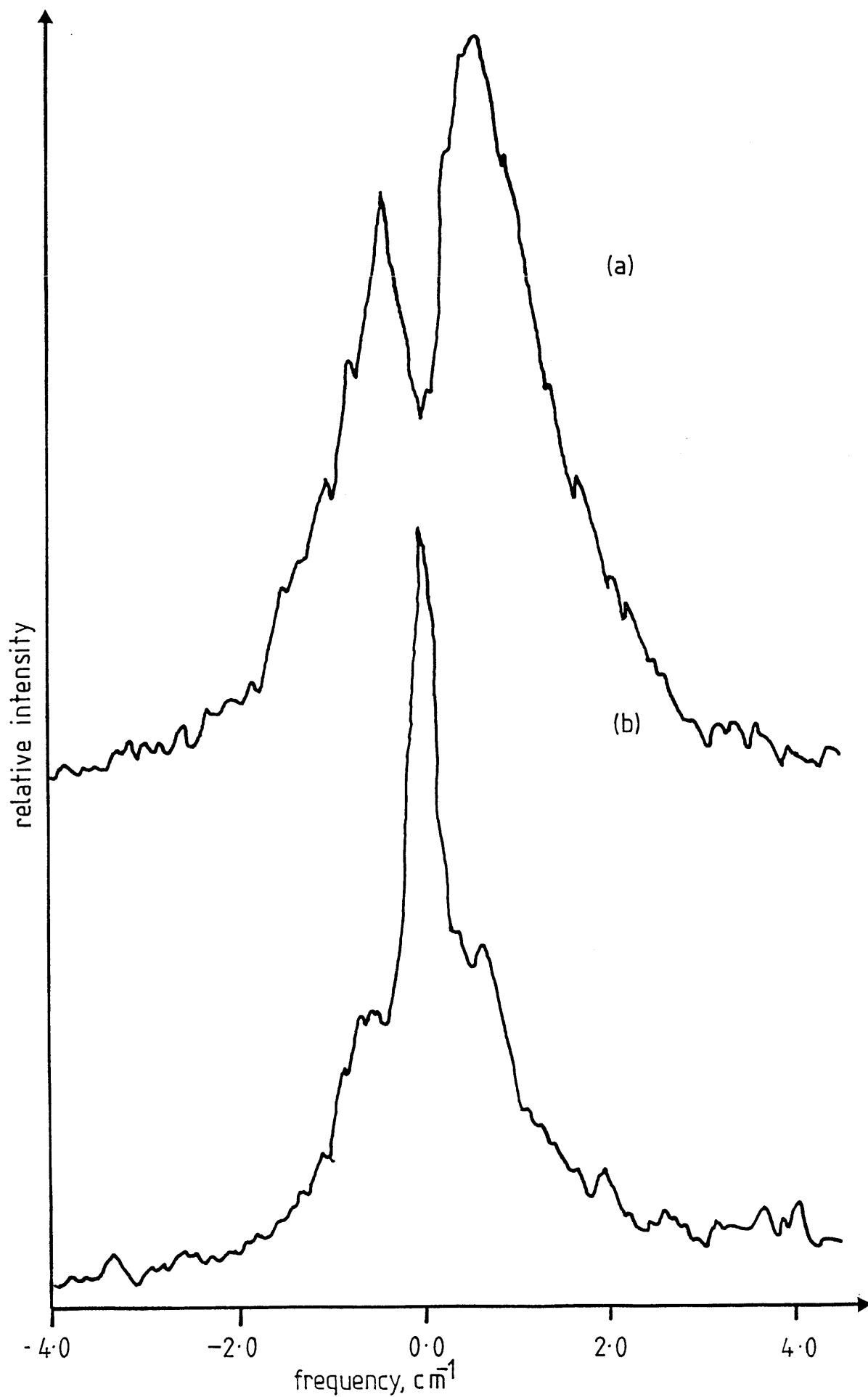
given.

i) 4-ABN-Ar

1:1 and 1:2 4-ABN-Ar complexes were observed with spectral shifts of -47cm^{-1} and -93cm^{-1} , respectively. Similar shifts of -53cm^{-1} and -98cm^{-1} were observed for aniline-Ar and aniline-Ar₂, respectively [20,29]. Rotational contours of the bare molecule origin and the 4-ABN-Ar origin are compared in figure 4.10. 4-ABN is a near symmetric top; the rotational constants calculated from the MNDO optimised geometry are $A = 0.1844$, $B = 0.0331$, $C = 0.0280$ (asymmetry parameter $K = -0.935$). The observed bare molecule rotational contour is characteristic of a perpendicular transition: the $S_1 \leftarrow S_0$ transition is short axis polarised. The rotational contour of 4-ABN-Ar, in contrast, shows a prominent Q branch. The argon atom is expected to lie above the plane of the aromatic ring the resulting complex is an asymmetric top and the transition moment now lies along the C axis. Similar characteristic C-type rotational contours have been observed for the aniline-Ar [20,29] and benzonitrile-Ar complexes [8].

The benzonitrile-Ar complex is bound mainly by a dispersive interaction between the Ar atoms and the π -electrons on the benzene ring. Due to the π -electron system extending towards the CN-group, the Ar atom is

Figure 4.10 Rotational contours of the 0_0^0 transitions of a) 4-ABN, bare molecule and b) 4-ABN-Ar complex.



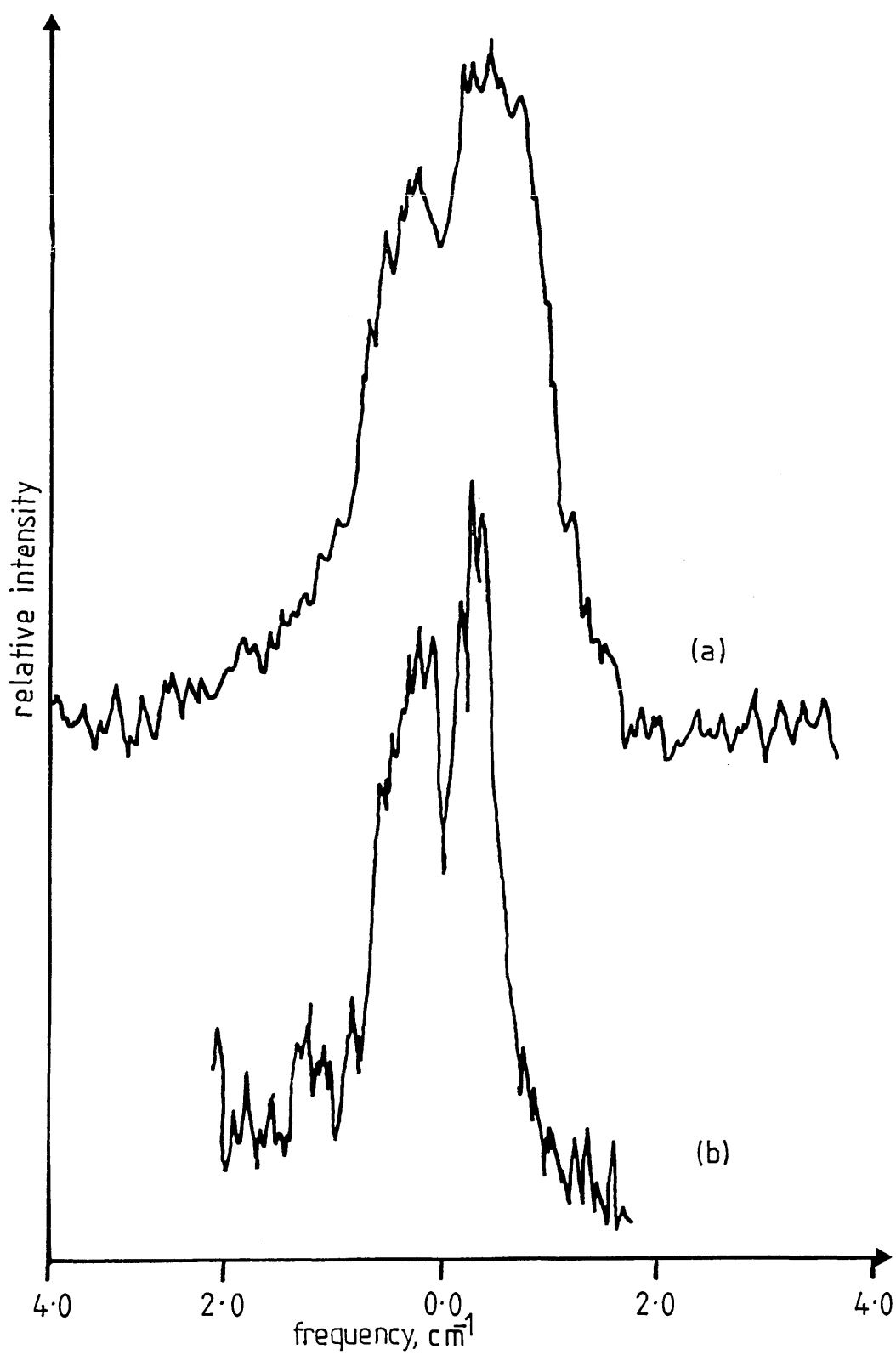
offset from the centre of the ring towards the CN-group. This trend is observed also in aniline-rare gas complexes [29]. In a series of 4-substituted benzenes the presence of a group which is a π -electron acceptor is likely to cause a decrease in electron density at the amino moiety as has been found experimentally [24] and theoretically [30]. This suggests that the 4-ABN-Ar complex will behave in much the same way as the benzonitrile-Ar complex: with the Ar atom shifting towards the CN-group.

ii) 4-ABN-RCN

1:1 complexes between 4-ABN and CH_3CN , $\text{C}_2\text{H}_5\text{CN}$ and $i\text{-C}_3\text{H}_7\text{CN}$ exhibited excitation features shifted $\sim 240\text{cm}^{-1}$ to the blue of the corresponding bare molecule features (see table 4.4). The results compare favourably with similar work conducted by Peng et al [31] on DMABN. They found a comparable value, 254cm^{-1} , for the DMABN/ CH_3CN complex. The rotational contours of the origin bands of the 4-ABN- CH_3CN and 4-ABN- $\text{C}_3\text{H}_7\text{CN}$ complexes are shown in figure 4.11; they have the same double-headed structure as the bare molecule (cf. figure 4.6) but with considerably reduced width.

Two types of interaction between 4-ABN and the nitriles can be envisaged: hydrogen bonding with the amino hydrogens or a dipole-dipole interaction. The former, hydrogen bonding, interaction is expected to give rise to a red spectral shift since $S_1 \leftarrow S_0$ excitation

Figure 4.11 Rotational contours of the 0_0^0 transitions of a) 4-ABN- CH_3CN and b) 4-ABN- $\text{C}_3\text{H}_7\text{CN}$ complexes.



of 4-ABN is accompanied by charge transfer from the amino group to the ring and a corresponding increase in the acidity of the amino protons. The observation of a blue shift can, however, be rationalised in terms of a dipole-dipole interaction between the ligand and the benzonitrile moiety, as previously shown for DMABN-solvent complexes. CNDO calculations [32] predict that in DMABN the local dipole on the benzonitrile group is reversed on excitation, leading to a decrease in the binding energy of the complex. Further MNDO calculations predict a similar change in charge distribution for 4-ABN on electronic excitation. The three nitriles all have similar dipole moments ($4+0.1D$) in the gas phase [33] and are therefore predicted to exhibit equal spectral shifts, as indeed observed.

The B-type rotational contours (figure 4.11) are consistent with a structure in which the ligand is associated with one of the para substituents, rather than lying above the plane of the ring (cf. 4-ABN-Ar). The narrowing of the rotational contour is consistent with a decrease of rotational constants on addition of the ligands, the heavier C_3H_7CN having a greater effect than the lighter CH_3CN .

Excitation features due to complexes of higher than 1:1 stoichiometry were not observed. Increasing the partial pressure of nitrile in the expansion certainly did not produce any excitation features to the red of the

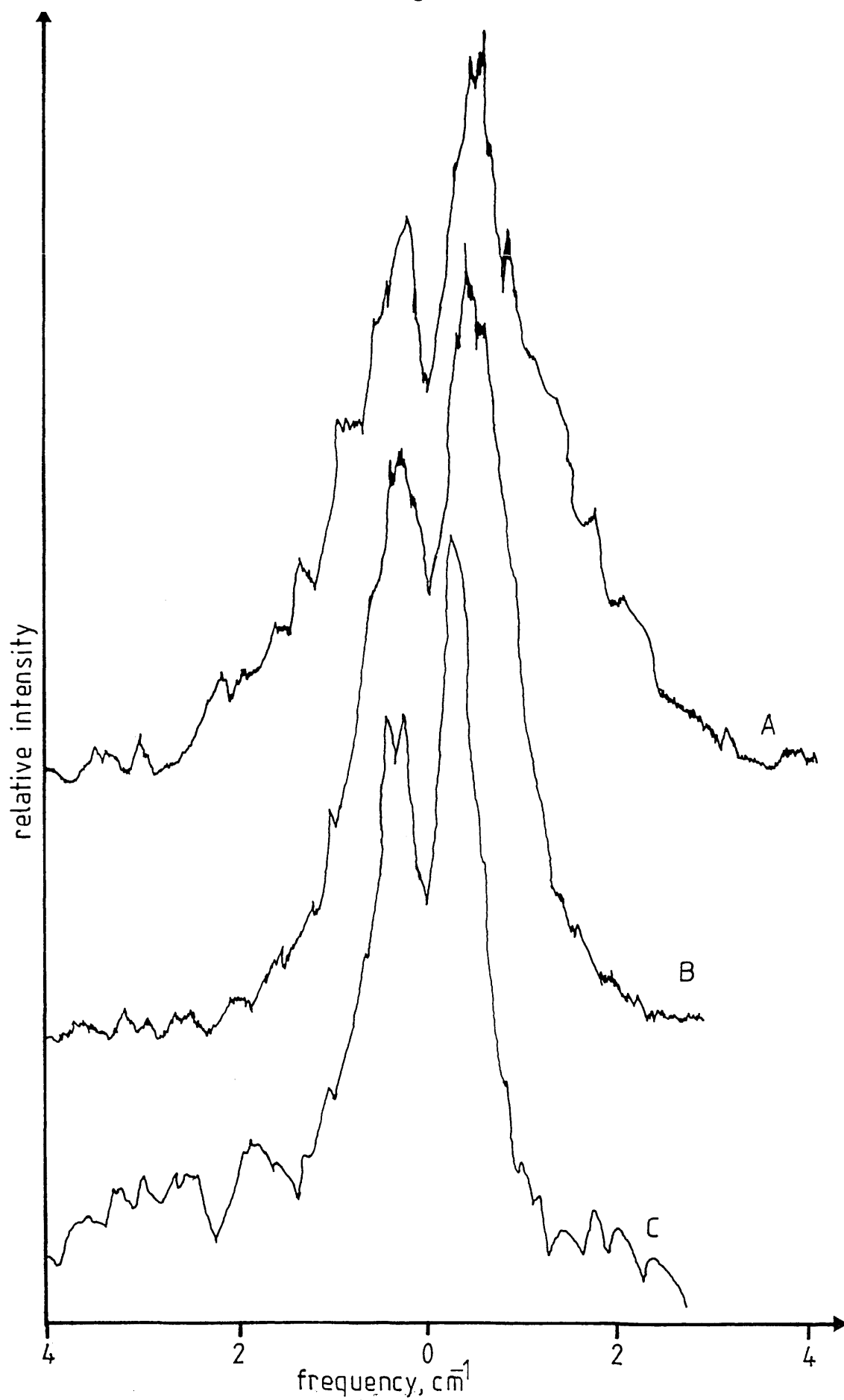
bare molecule origin; excitation features to the blue of the 1:1 complex bands may have been present but obscured by the bare molecule spectrum.

iii) 4-ABN-H₂O

On addition of water vapour to the expansion, three excitation bands appeared to the high energy side of the bare molecule features, as shown in figure 4.8(b). All three peaks showed a linear dependence of intensity on partial pressure of water vapour in the range 2-12 mBar H₂O; at higher partial pressures (~12-23mBar) a "saturation" effect was observed and the intensities reached maximum limiting values. All three excitation features can therefore be attributed to 1:1 complexes; no features due to complexes of higher stoichiometry were observed. The rotational contours of the three "origin" complex features are shown in figure 4.12. All show a B-type structure but with clearly different widths, indicating that each is due to a different geometric isomer.

Water may hydrogen bond to the cyano group of 4-ABN, to the amino nitrogen or to the protons. As discussed above, the latter type of interaction is expected to give rise to a red shift whereas the former lead to blue shifts. MNDO calculations were performed to assess the relative stabilities of some probable complex geometries involving interaction with the cyano group or

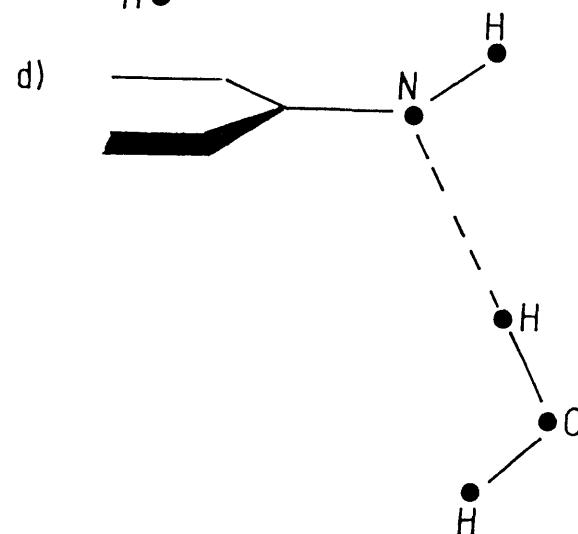
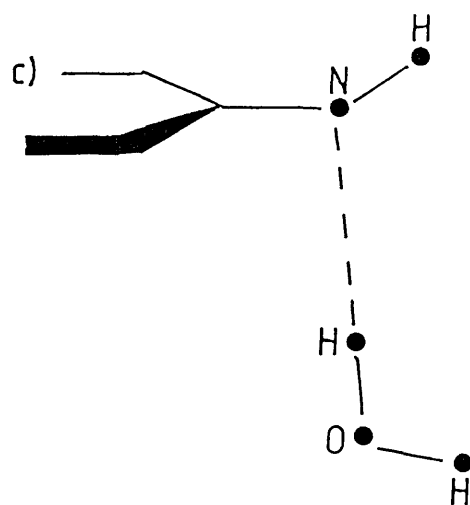
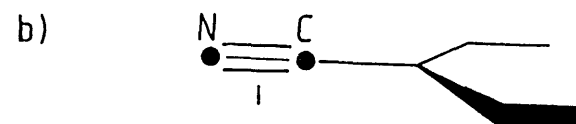
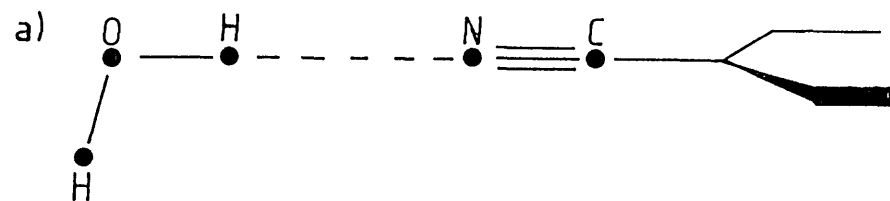
Figure 4.12 Rotational contours of the 4-ABN-H₂O excitation features occurring at a) 84 cm⁻¹, b) 196 cm⁻¹ and c) 314 cm⁻¹ (as shown at low resolution in figure 4.9b).



the amino nitrogen. Four examples of stable geometries are shown in figure 4.13. As depicted in figure 4.12(a) and (b) there are two obvious alternative structures for H_2O interacting with the cyano group; the linear structure shown in (a) is predicted to be the more stable of the two. The water molecule may be able to take up a large number of configurations in interacting with the amino nitrogen. Two possible geometries are illustrated in figure 4.13(c) and (d); both are predicted to be stable, with the "cis" structure (d), in which the water molecule is swung round towards the ring, being the more stable. For all four structures shown the calculated hydrogen bond length lies in the range 2.6-2.8 Å.

The complex exhibiting the smallest spectral shift (84cm^{-1}) has the broadest rotational contour, most similar to that of the bare molecule. It seems likely, therefore, that this complex has a structure of the form shown in figure 4.13(a). The intermolecular interaction responsible for the blue shift in this case is assumed to be dipole-dipole in nature, analogous to that discussed for the nitrile complexes. (Little change in the electron density on the cyano nitrogen is expected on excitation and hence little change in the strength of the hydrogen bonding interaction). On the basis of the relative dipole moments of water (1.85D) [33] and the nitriles (4.0D) [33] a shift of approximately 110cm^{-1} would be predicted for this complex.

Figure 4.13 Schematic representation of MNDO optimised geometries of 4-ABN-H₂O complexes. In b), c) and d) the water molecule lies below the plane of the ring.



The other two 4-ABN-H₂O isomers probably involve association of the water molecule with the amino lone pair, with structures similar to those in figure 4.13(c) and (d).

iv) 4-ABN-CH₃OH

As shown in figure 4.9(c) addition of a small partial pressure (~5mBar) of methanol to the expansion is accompanied by the appearance of six new features to the high energy side of the bare molecule features. All of these features appeared to be due to complexes of 1:1 stoichiometry. The bands at 92, 210 and 305cm⁻¹ probably correspond to complexes similar in structure to the three formed between 4-ABN and water as discussed. The rotational contours of these peaks are similar in shape to those observed for 4-ABN-H₂O and show a similar decreasing trend in width with increasing spectral shift. The weaker features between 210 and 305cm⁻¹ may be due to transitions involving low frequency vibrations of the 210cm⁻¹ complex.

v) 4-ABN-CHCl₃

1:1 complexes between 4-ABN and CHCl₃ behave similarly to the 4-ABN-RCN complexes. Excitation features were produced that were blue shifted by 128cm⁻¹ from the bare molecule features. The rotational contour was reduced in band width but exhibited the same double-

headed structure as the origin. The nature of the interaction is thought to be dipole-dipole and is based on the same reasoning as applied to 4-ABN-RCN. However, the possibility of a hydrogen-bonded interaction cannot be ignored. For example, with fluorobenzene/ CCl_4 complexes, red-shifted spectral features are observed where the nature of the interaction was thought to be dispersive [34]. However, the fluorobenzene/ CHCl_3 complex give rise to a blue-shifted spectral feature, 117cm^{-1} , where the complex is thought to be hydrogen-bonded [34].

4.3.3 Dispersed fluorescence spectra of 4-ABN complexes

Dispersed fluorescence spectra resulting from excitation of the origins of 4-ABN complexes revealed the same features as the bare molecule origin dispersed fluorescence spectrum. Figure 4.14 shows the dispersed fluorescence spectra of the 4-ABN- H_2O upon 0_0^0 excitation of the complex peaks. The spectra 4.14(b) are practically identical to spectrum 4.14(a), recorded under the same resolution, excepting the spectral shift of each band. The resolution was lower than for recording the bare molecule dispersed fluorescence spectra because of the lesser intensity of the complex peaks. Although small bands do appear in the complex spectra in addition to those found in the bare molecule they were only partially resolvable in 4-ABN- CHCl_3 and - CH_3CN as exhibited by figure 4.15 with 4-ABN- CH_3CN on 0_0^0

Figure 4.14 Dispersed fluorescence spectra of a) 4-ABN, bare molecule $\lambda_{\text{ex}} 0^\circ$ and b) 4-ABN- H_2O complex $\lambda_{\text{ex}} 84, 196$ and 314 cm^{-1} .

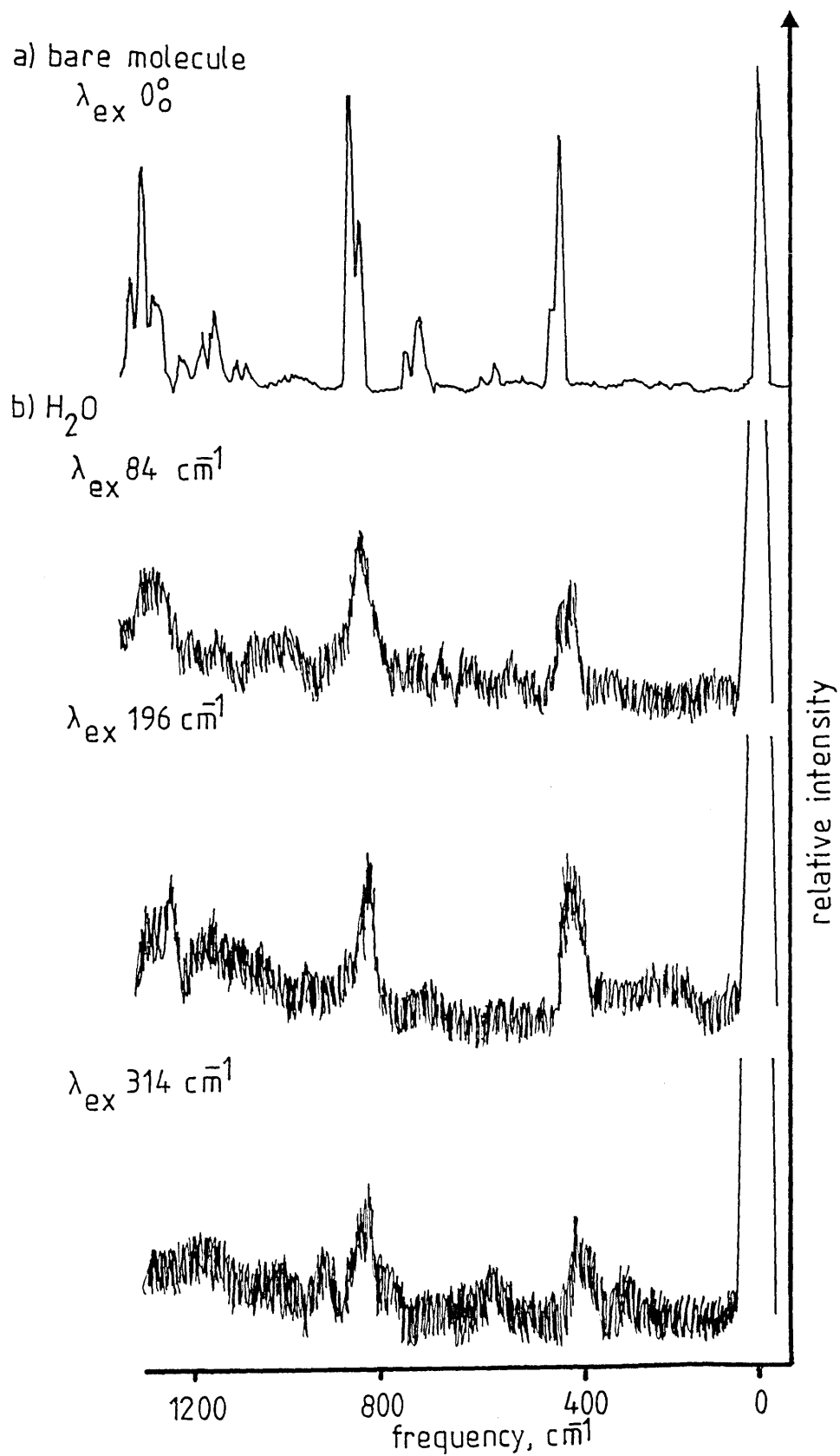
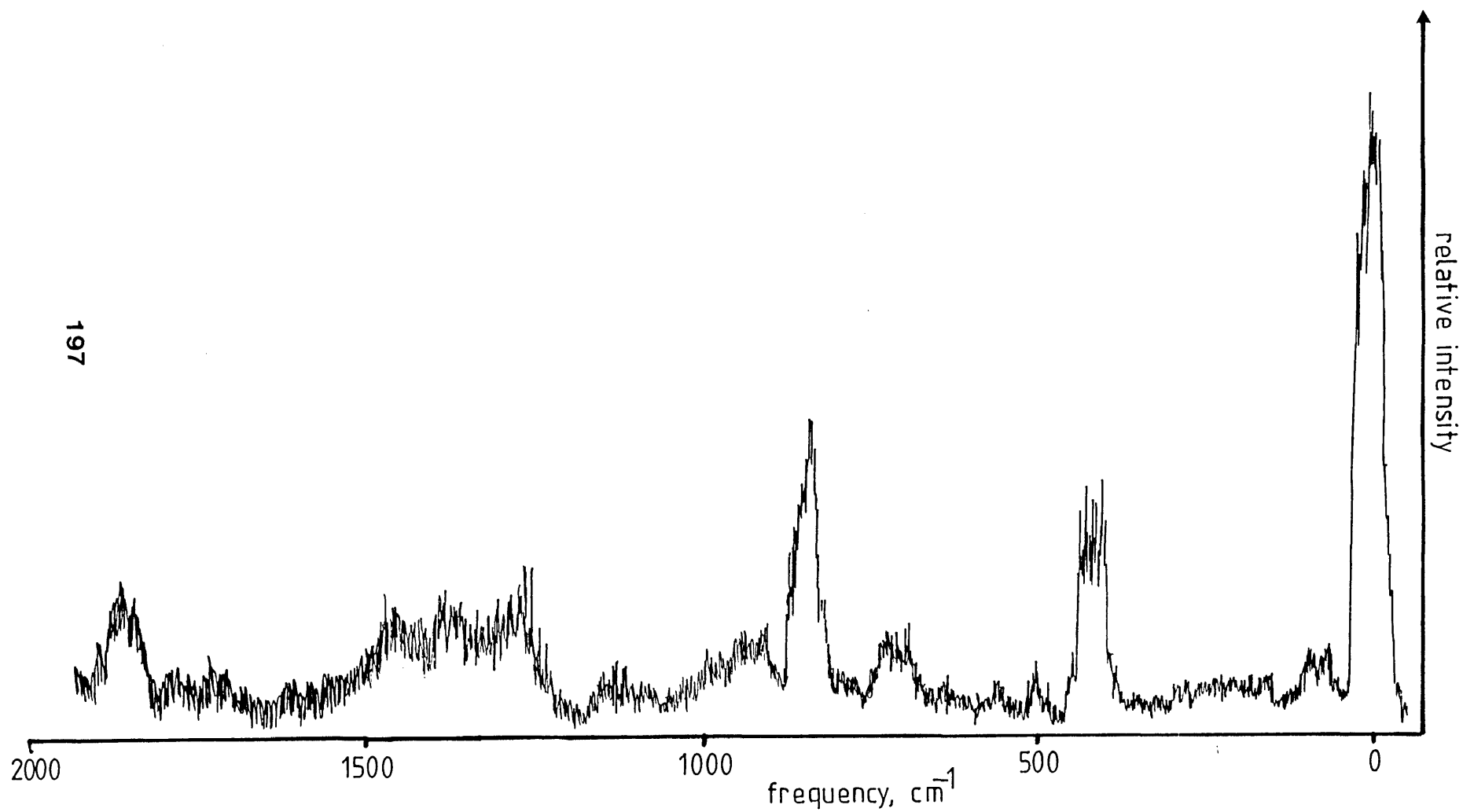


Figure 4.15 Dispersed fluorescence spectra of 4-ABN-CH₃CN complex, λ_{ex} 236 cm⁻¹.



excitation. The transitions were too weak to evaluate reliable vibrational frequencies but the approximate values are given in table 4.5 . These small bands have been attributed to van der Waals mode vibrations in the electronic ground state in the case of benzonitrile complexes [35].

4.3.3 Fluorescence decay lifetimes

The fluorescence decay lifetimes, τ_f for selected vibronic transitions of 4-ABN and for the respective complexes are listed in table 4.6.

The time-resolved emission of states at excess vibrational energies, $E_v = 0 - 1164\text{cm}^{-1}$ was investigated. A typical experimental decay curve is presented in figure 4.16.

The fluorescence lifetimes for the selected vibronic levels are listed in table 4.6(a). All exhibited single exponential decay over the E_v range studied. τ_f for the 0_0^0 is 14.4ns and is approximately 4x greater than found in a non-polar solvent at room temperature where τ_f is 3.3ns in hexane with a fluorescence quantum yield, ϕ_f of 0.14 and a radiative decay rate, k_f , of 4.1×10^{-7} seconds. The phosphorescence quantum yield, ϕ_p , is 0.64 and ϕ_f is 0.36 in n-butylchloride/2-methylbutene at 77K indicating that intersystem crossing is the dominant non-radiative decay rate [36] for this molecule. Figure 4.17 shows a plot of

Table 4.5 Assignment of the dispersed fluorescence spectrum of the 4-ABN-acetonitrile complex, 0_0^0 excitation.

0_0^0 excitation				Ass
4-ABN-CH ₃ CN		4-ABN		
$\Delta\nu/\text{cm}^{-1}$	RI	$\Delta\nu/\text{cm}^{-1}$	RI	
0	100	0	100	0_0^0
82	14			
420	46	421	31	$6a_1^0/I_2^0$
711	14	705	18	I_2^0X
840	60	832	84	$6a_2^0/6a_1^0I_2^0$
921	16			
1259	14	1252	33	$6a_1^0I_2^0$
1354	14			
1695	26	1688	35	$6a_1^09a_1^0$

RI = relative intensity

Ass = assignment

Table 4.6 Fluorescence decay lifetimes of a) 4-ABN (where $\chi^2 < 1.1$) and b) 4-ABN-complexes (where $\chi^2 < 1.3$)

a)

frequency cm ⁻¹	τ_f ns
0	14.4
382	13.4
493	12.8
678	12.8
815	11.4
1164	10.2

b)

solvent	frequency* cm ⁻¹	τ_f ns
acetonitrile	236	13.4
chloroform	128	14.0
water	196	14.5
	314	13.5

* Relative to the bare molecule 0%.

Figure 4.16 Fluorescence decay curve for the 0_0^0 transition of 4-ABN.

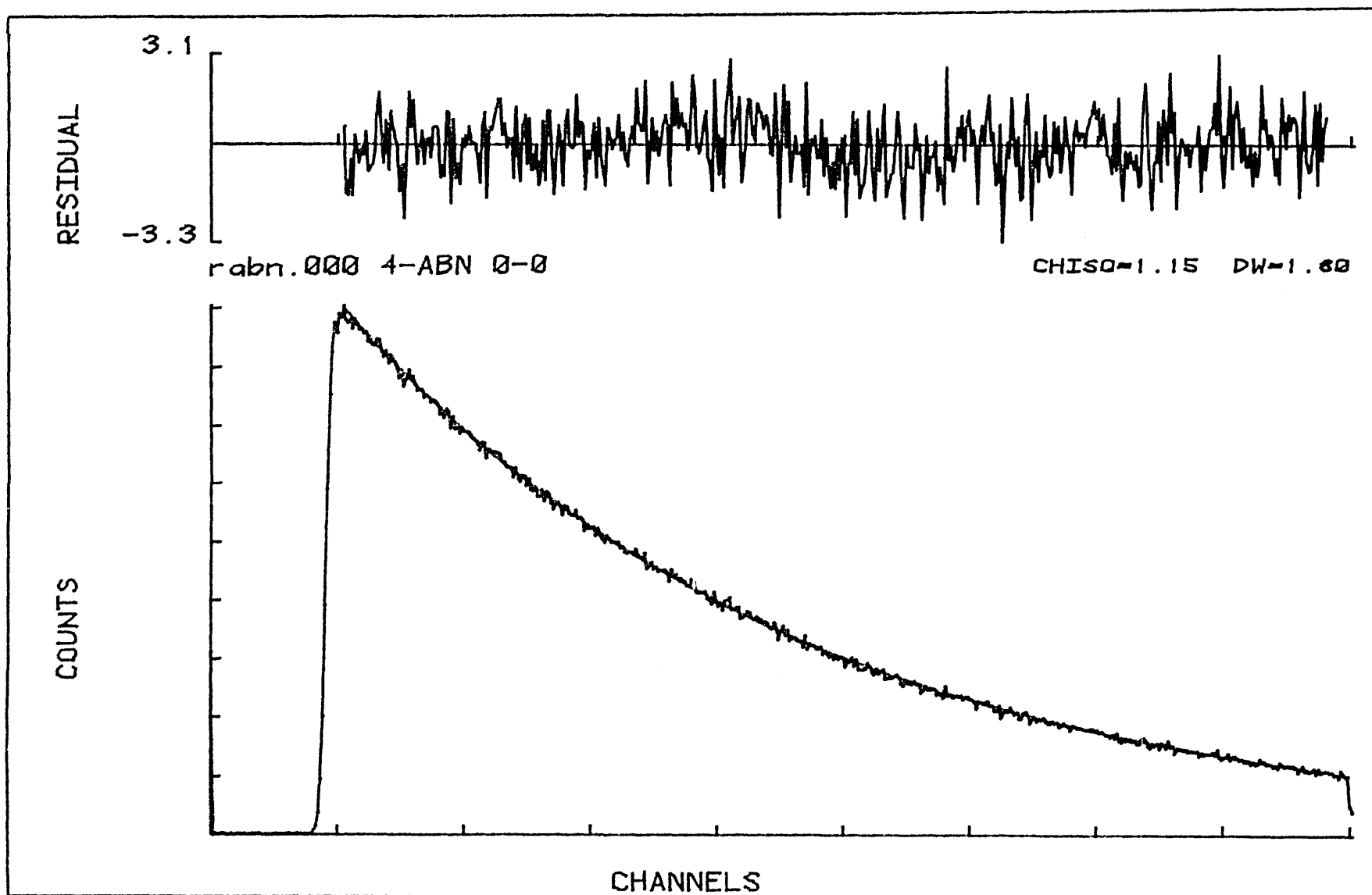
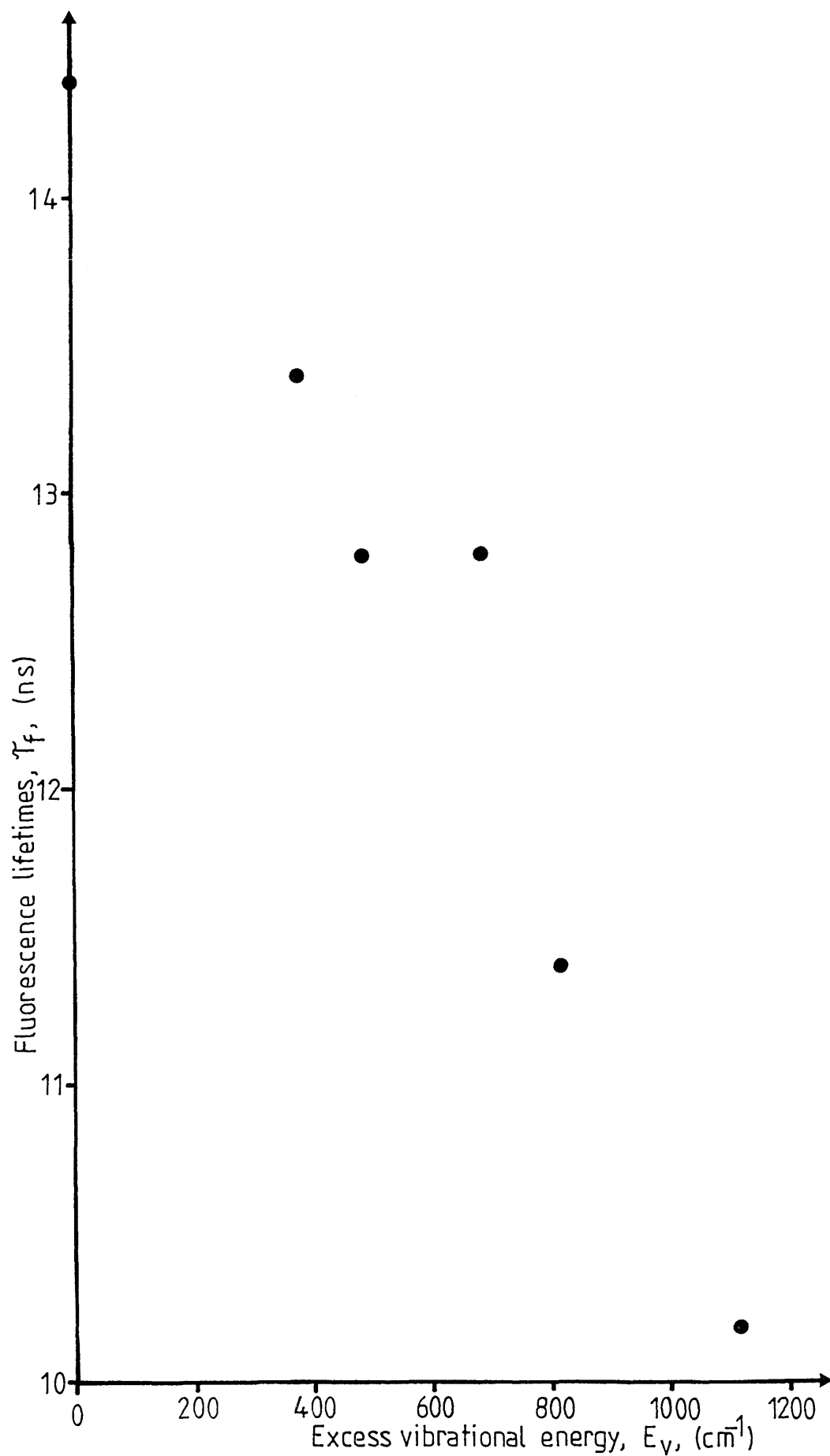


Figure 4.17 Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for selected excited single vibronic levels of 4-ABN.

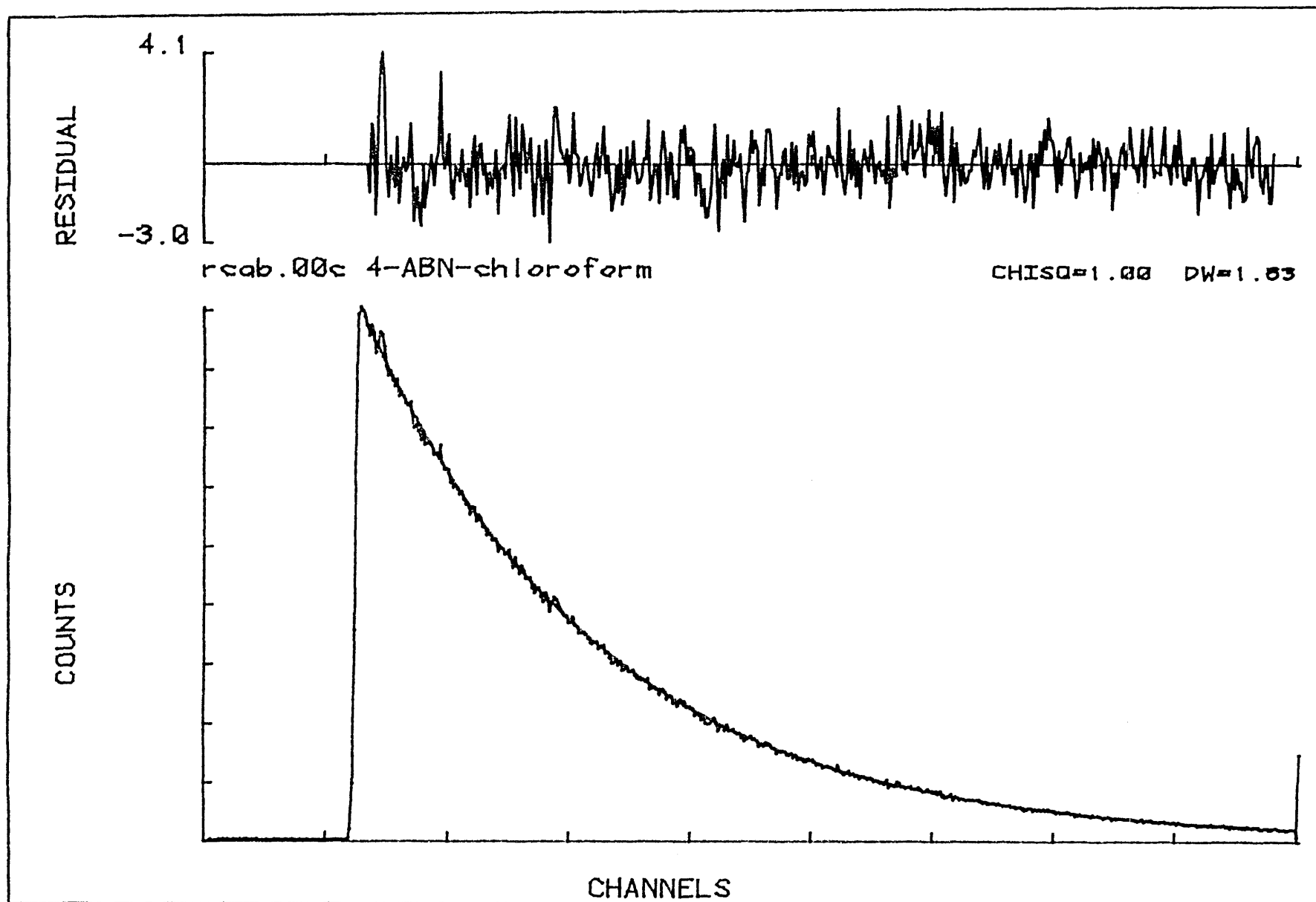


τ_f versus E_v . It can be seen that τ_f decreases uniformly and fairly rapidly with increasing E_v . There is no evidence of intramolecular vibrational redistribution (IVR) in the dispersed fluorescence spectra (figure 4.7 and 4.8) which suggests that the increase in decay rate with E_v is promoted by the optically populated vibration. In the case of such molecules as 4-difluorobenzene [37] and 4-fluorotoluene [38], the threshold for IVR is thought to occur at 1760cm^{-1} and 1590cm^{-1} respectively for a vibrational temperature of 300K. This suggests that IVR will occur at higher E_v than studied here. In the region where $E_v > 1365\text{cm}^{-1}$, that is in a high energy domain, the electronic relaxation rate is expected to exhibit a weak dependence on the excess vibrational energy.

In aniline, the Φ_f of the 0_0^0 transition is approximately 0.5 [22] and the fluorescence lifetime is 7.9ns when measured in the gas phase (0.25 torr). The fluorescence lifetime was not strongly dependent upon the vibronic excitation band within the first 1000cm^{-1} of the absorption spectrum. 4-ABN appears to behave similarly to benzonitrile. In benzonitrile, the solution phase τ_f measured in a simple diene solution at room temperature is 9.6ns [39] which is approximately 7x less than that for the 0_0^0 transition in the cold isolated molecule, 67ns [8]. The τ_f over the E_v range studied for benzonitrile also decreased significantly.

The fluorescence τ_f for the 4-ABN complexes exhibit mono-exponential decay. A typical experimental decay curve for the 4-ABN-CHCl₃ complex is given in figure 4.18. As shown with DMABN (Chapter 3), the fluorescence lifetimes do not deviate dramatically from the bare molecule τ_f .

Figure 4.18 Fluorescence decay curve of the 4-ABN-CHCl₃ complex.



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CHAPTER 5

SPECTROSCOPY OF JET-COOLED AROMATIC AMINES

CHAPTER 5

SPECTROSCOPY OF JET-COOLED AROMATIC AMINES

5.1 INTRODUCTION

Incorporated in this chapter is a summary of the spectroscopic properties of the aromatic amines studied so far: 4-N,N-dimethylaminobenzonitrile (DMABN), and 4-aminobenzonitrile (4-ABN). Deductions are illustrated by preliminary studies on further aromatic amines: N,N-dimethylaniline (DMA), N-methylaniline (NMA), 2-aminobenzonitrile (2-ABN) and 3-aminobenzonitrile (3-ABN). The aim of this chapter is to develop a clearer understanding of the large amplitude motions of the amino group and their effect on the spectroscopy of the molecule. For large polyatomic molecules, such as the aromatic amines studied here, the information regarding the large amplitude motions such as methyl internal rotation, N-inversion and C-N torsions is limited for the ground state and virtually non-existent in the excited state [1].

5.1.1 N-inversion

An account of N-inversion is given in Chapter 4, section 4.1.1. Early work on ring substituted anilines has shown that electron withdrawing substituents lower the barrier to inversion [2] and decrease the dihedral angle [3], presumably by decreasing the electron

density in the nitrogen lone pair while electron donating substituents have the opposite effect [3]. Since the methyl group is normally considered to be electron donating relative to hydrogen, a conclusion supported by upfield shifts relative to aniline observed in ^{15}N NMR studies of liquid N-methylaniline (NMA) [4], microwave results that have been reported in the literature for NMA and DMA [5-8] are somewhat contradictory.

5.1.2 Internal rotation of the CH_3 group

The internal rotation of CH_3 is expected to change greatly on excitation. The knowledge of this change is limited [1]. The potential for internal rotation of a CH_3 group in a planar molecule is expressed by:

$$V(\theta) = 1/2 V_3(1-\cos 3\theta) + 1/2 V_6(1-\cos 6\theta) \quad 1$$

where θ is the angle of rotation of the CH_3 group about the top axis measured from a reference configuration of the CH_3 group. The potential for internal rotation is, therefore, represented by V_3 and V_6 , and by the barrier height to the internal rotation. When the barrier height is 0, the energy levels associated with the internal rotation coincide with those of a one-dimensional free rotor and are given by Bm^2 . B is the rotational constant of the CH_3 group and m the rotational quantum number. In the case of non-zero barrier heights, the energy levels become irregular and

give rise to tunnelling effects. The levels are usually denoted by a combination of the rotational quantum number, m , of a one-dimensional free rotor and the symmetry species of the permutation inversion group isomorphous to the CH_3 group.

The above equation only applies to a planar molecule. Though DMABN and DMA are denoted as belonging to the C_{2v} point group, planarity is lost because of the inversion vibration of the nitrogen atom making the potential for one, let alone two methyl groups extremely complicated to determine.

NMA

In NMA there are three large amplitude vibrations of the HNCH_3 group, the torsion of this whole group around the bond between the nitrogen atom and the ring, the torsion of the methyl group and the inversion of the amino group. Other vibrations will also be active in the low energy region (for example, the the whole NCH_3 unit wagging out of the ring plane). But the amplitude of these modes is not expected to be large [7].

NMA is a prolate asymmetric rotor belonging to the C_s point group. The inversion about the amino group is still thought to invoke a double minimum potential [5].

DMA

DMA is also a prolate asymmetric rotor but it belongs to the C_{2v} point group. Substitution of a second methyl group on an atom generally leads to an increase in the barrier to methyl rotations but no splittings of similar transitions were observed in NMA [5]. Two equivalent methyl groups usually give rise to triplets or quartets when splittings are observed.

5.2 EXPERIMENTAL

The compounds NMA, 2-ABN and 3-ABN were all purchased from Aldrich ltd and were used as found. Oven temperatures used were 45, 110 and 105°C respectively. Backing pressures of 3-4Bar of helium were used in conjunction with a 97 μ m nozzle.

5.3 RESULTS AND DISCUSSION

5.3.1 Large amplitude motions of the amino group

5.3.1a DMA

The fluorescence excitation spectrum of DMA is shown in figure 5.1b. The spectrum appears to resemble that of DMABN as discussed in Chapter 3. The 0_0^0 is at 32973cm⁻¹. There is no intense origin and the molecule exhibits similar types of progressions as denoted in

Figure 5.1 Fluorescence excitation spectra of a) NMA and b) DMA.

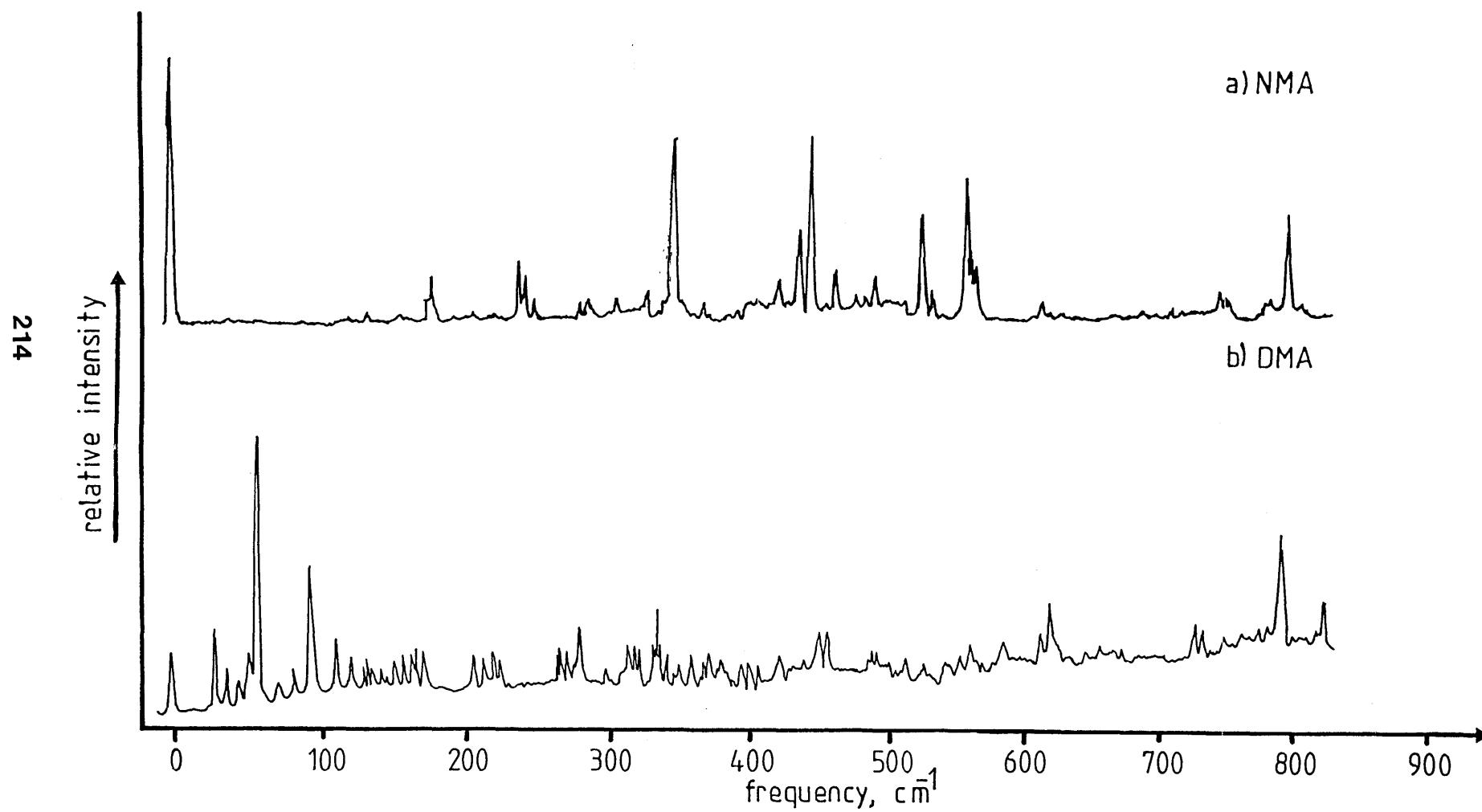


figure 5.2b. The relative quantum yield appeared to be approximately an order of magnitude less than that for DMABN and for 4-ABN. The structure was also much more complicated than observed for DMABN and so only one fundamental vibration of benzene, 1, at 723cm^{-1} (see Chapter 1 section 1.6) could be well resolved. This is listed in table 5.1a along with those for DMABN as a comparison. There is possibly another fundamental at $\sim 272\text{cm}^{-1}$.

In microwave experiments carried out by Cervallati et al [8], the angle θ of the amino group relative to the plane of the aromatic ring, was given as 27° compared to bulk dielectric constant dipole-moment measurements [9] which gives $\theta = 29.5^\circ$ whilst Kerr constant data [10] gives $\theta < 20^\circ$. From electron diffraction data, the $\text{CH}_3\text{N}^{\wedge}\text{CH}_3$ angle is given as 116° which suggests little deviation from the planarity of the N atom. Though there is some disagreement about θ , the general view is that it should be less than for aniline [11,12]. The lower value of θ compared to aniline and the fact that the $0^+ - 0^-$ energy separation is only 3cm^{-1} suggest that the barrier to inversion is lower than in aniline (6.3kJmol^{-1}). Calculations by Cervellati et al predicted a barrier of $1\text{-}3\text{kJmol}^{-1}$. It also appears that the $\text{N}(\text{CH}_3)_2$ torsional frequency is less than 100cm^{-1} and may be as low as 50cm^{-1} . The barrier to internal rotation about the N-aryl bond would therefore appear to

Table 5.1 Assignments of DMABN, DMA and NMA fluorescence excitation spectra.

DMABN		DMA		Ass
$\bar{\nu}$, cm ⁻¹	RI	$\bar{\nu}$, cm ⁻¹	RI	
0	15	0	23	0 ₀ ⁰
37	11	30	39	a ₀ ¹
42	8	47	9	b ₀ ¹
61	100	60	100	c ₀ ¹
99	65	96	50	d ₀ ¹
117	23	124	14	e ₀ ¹
780	17	724	8	1 ₀ ¹
818	5			1 ₀ a ₀ ¹
823	6	772	8	1 ₀ b ₀ ¹
840	25	785	23	1 ₀ c ₀ ¹
880	14			1 ₀ d ₀ ¹
898	9	821	12	1 ₀ e ₀ ¹

NMA							
$\bar{\nu}$, cm ⁻¹	RI	$\Delta\bar{\nu}$, cm ⁻¹	Ass	$\bar{\nu}$, cm ⁻¹	RI	$\Delta\bar{\nu}$, cm ⁻¹	Ass
0	100		0 ₀ ⁰	280	19		(6a ₀ ¹)
154	28	154	v ₀ ¹	433	69	153	v ₀ ¹
161	17	7	w ₀ ¹	440	90	7	w ₀ ¹
178	88	17	x ₀ ¹	458	23	18	x ₀ ¹
205	15	27	y ₀ ¹	485	12	27	y ₀ ¹
239	12	34	z ₀ ¹	517	98	32	z ₀ ¹

$\bar{\nu}$ = frequency
 RI = Relative Intensity
 Ass = Assignment

be similar to barriers to internal rotation for planar benzene derivatives ($12 < V_2 < 19 \text{kJmol}^{-1}$). The abundance of such low frequency modes makes the assignment of the DMA spectrum extremely complicated.

5.3.1b NMA

The 0_0^0 transition occurs at 33302cm^{-1} and is intense. The fluorescence excitation spectrum is given in figure 5.1a. There appeared to be little of the density of structure in the origin region as observed for DMA under the experimental conditions used, though the spectrum is still quite complicated in the middle energy region. An attempt was made to define a similar series of progressions as observed with DMA. There did not appear to be any with correlating intensities but one progression from the origin region is indicated in table 5.1b. It recurred at 280cm^{-1} but the intensities appear to oppose each other excepting in the case of y_0^1 .

In microwave spectra, absorptions associated with the torsional vibration of the methyl group appear as a sequence of sharp lines with the fundamental around 200cm^{-1} [8]. The HNCH_3 torsion occurs below 100cm^{-1} where there is a strong band at 71cm^{-1} and is taken to be the fundamental due to the HNCH_3 torsion and not to the inversion because it is not affected by deuteration. The barrier to internal rotation appears to decrease on going from solution to vapour phase, as shown by being

observed in NMR experiments [13,14]. It is given as 14.5kJmol^{-1} and is a little lower than in aniline at 24kJmol^{-1} and fluoroaniline 19kJmol^{-1} [15]. The magnitude of this barrier reflects the conjugation between the lone pair on the nitrogen atom and on the ring.

The NMA inversion is assigned to 42.5cm^{-1} in the infrared spectrum, although no lines are separated by 42.5cm^{-1} higher up in the spectrum. The estimated barrier to inversion 2.3kJmole^{-1} . The results from Cervellati et al [8] predict that NMA is more planar at the nitrogen atom than in aniline itself which has an inversion barrier of 6.3kJmol^{-1} . Because the CH_3 group is electron donating compared to H, a simple argument suggests that lone pair electron density on the N atom is greater in NMA than in aniline itself and thus the conformation is more pyramidal. This is apparently not the case, there are two hypotheses for the lowering of the inversion barrier of NMA relative to aniline.

1) Note that whilst NMA is more planar at the nitrogen atom than aniline the barrier to torsion about the N-aryl ring is less than in aniline. With ring substituted anilines, a lower barrier to torsion would indicate less conjugation between the nitrogen lone pair and the ring and hence more pyramidal about the nitrogen atom as seen in 4-fluoroaniline [15,16]. The differing behaviour of NMA might result from the lone pair on the

nitrogen being delocalised partially into the N-C (methyl) bond as has been postulated elsewhere for other molecules [17]: the methyl group can act as an electron acceptor, relative to hydrogen in the presence of a lone pair on the adjacent atom.

2) Ab-initio computations on aniline and NMA show that the effect of replacing an amino hydrogen atom by a methyl group is to enhance the donation of π -charge to the benzene ring. This enhancement to the ring has been identified with the lowering of the barrier to inversion [15,16]. In the case of NMA this is regarded as hyperconjugation of the methyl group. It is interesting to note that the effect of substituting the 4-hydrogen of aniline by a methyl group is to lead to the increase in the inversion barrier [18] as predicted by Here et al [19].

The above may be extended to dimethyl substitution of the amino group to account for the further lowering of the inversion barrier in DMA. The presence of the cyano group in DMABN has the effect of increasing the inversion barrier in the amino group relative to DMA. This is expected to be much less than in aniline, hence, the abundance of low frequency modes in the fluorescence excitation spectrum (figure 5.2a) and in dispersed fluorescence spectrum (figure 3.4). The calculations of Rettig [20] supplement these points as shown in table 5.2 with the discussed microwave data and

Figure 5.2 Fluorescence excitation spectra of a) DMABN, b) DMA and c) 4-ABN. Two frequency of 60 cm^{-1} are indicated by ● and ◆.

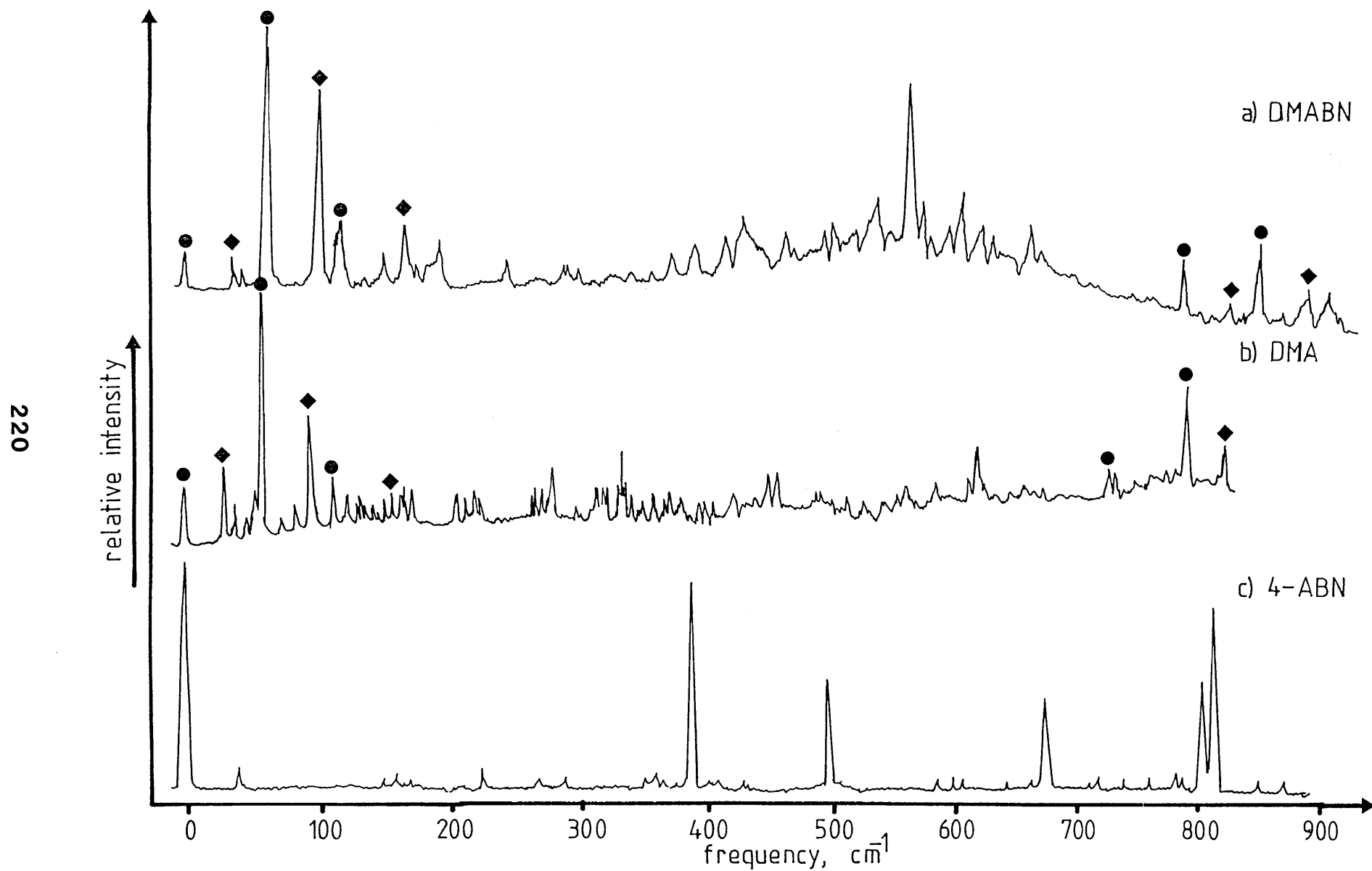


Table 5.2 Ground state assignment of some of the large amplitude motions of DMABN and 4-ABN.

	Aniline [21]	NMA [8]	DMA [20,(5)]	DMABN	4-ABN
Barrier to inversion, cm^{-1}	450	190	65-80 (1-3 kJmol^{-1})		
I_2 , cm^{-1}	427				430
N-aryl torsion, cm^{-1}	277	71	15-30 (~15 kJmol^{-1})		
N-CH ₃ torsion, cm^{-1}			115-130 (50-100)	116	

with relevant assignments from this work given for DMABN and 4-ABN.

Due to the density of bands in the dispersed fluorescence spectra a highly resolved spectrum is difficult to obtain due to limitations of the resolution of the monochromator. A method by which the ground state potentials could be more accurately determined is by stimulated emission spectroscopy (ionisation dip and fluorescence dip spectra) [1] which requires the use of two colour lasers. (It would now be possible to carry out such an experiment in our laboratory due to the recent acquisition of a Coherent Nd-Yag pumped dye laser system.)

5.3.2 Spectroscopy of 2-ABN, 3-ABN and 4-ABN

As in aniline, low energy vapour phase infrared spectra of substituted anilines are dominated by transitions in the inversion vibrations of the amino-group. The potential energy barrier to inversion is of interest because its height will be related to the electron distribution on the amino nitrogen and the benzene ring and to the non-planarity of the amino fragment [22].

The effect of 4-substitution of aniline with a cyano group has been covered in Chapter 4; it leads to a slight increase in the N-inversion barrier. The effect of 2-, 3- and 4-halogen substitution in aniline has been

studied by Kydd and Krueger [18] in the vapour phase in the far infrared region. Their deductions with regard to substitution are somewhat inconclusive. In the 2-, 3- and 4-fluorotoluenes (FT) studied under supercooled conditions it was found the barrier to methyl rotation was much increased, on excitation, in 2- and 3-FT than expected [23] for simple systematic substitution. In 2-FT, hydrogen bonding in the ground state between the H atom of the methyl group and the F atom is considered to be weak. On excitation, however, it is possible that H-bonding is enhanced due to the change in charge densities of the two substituents. Also, the effect of steric hindrance to the barrier to methyl rotation has to be taken into account.

In 3-FT the effects of steric hindrance and H-bonding are negligible. On excitation, the rotation barrier is greatly increased. This is accounted for by the fact that hyperconjugation of the methyl group attached to the 3-C atom may occur [23]. With these thoughts in mind, a preliminary study of 2- and 3-ABN was made.

Figure 5.3 gives the fluorescence excitation spectra of 2-ABN, 3-ABN and 4-ABN. The origin for the spectra are 31276, 31698 and 33493 cm^{-1} respectively. Tentative assignments are given in table 5.3 for 2-ABN and 3-ABN based on shifts found in fluoro-toluenes [23] and Varsanyi's suggested shifts for benzene derivatives

Figure 5.3 Fluorescence excitation spectra of a) 2-ABN, b) 3-ABN and 4-ABN.

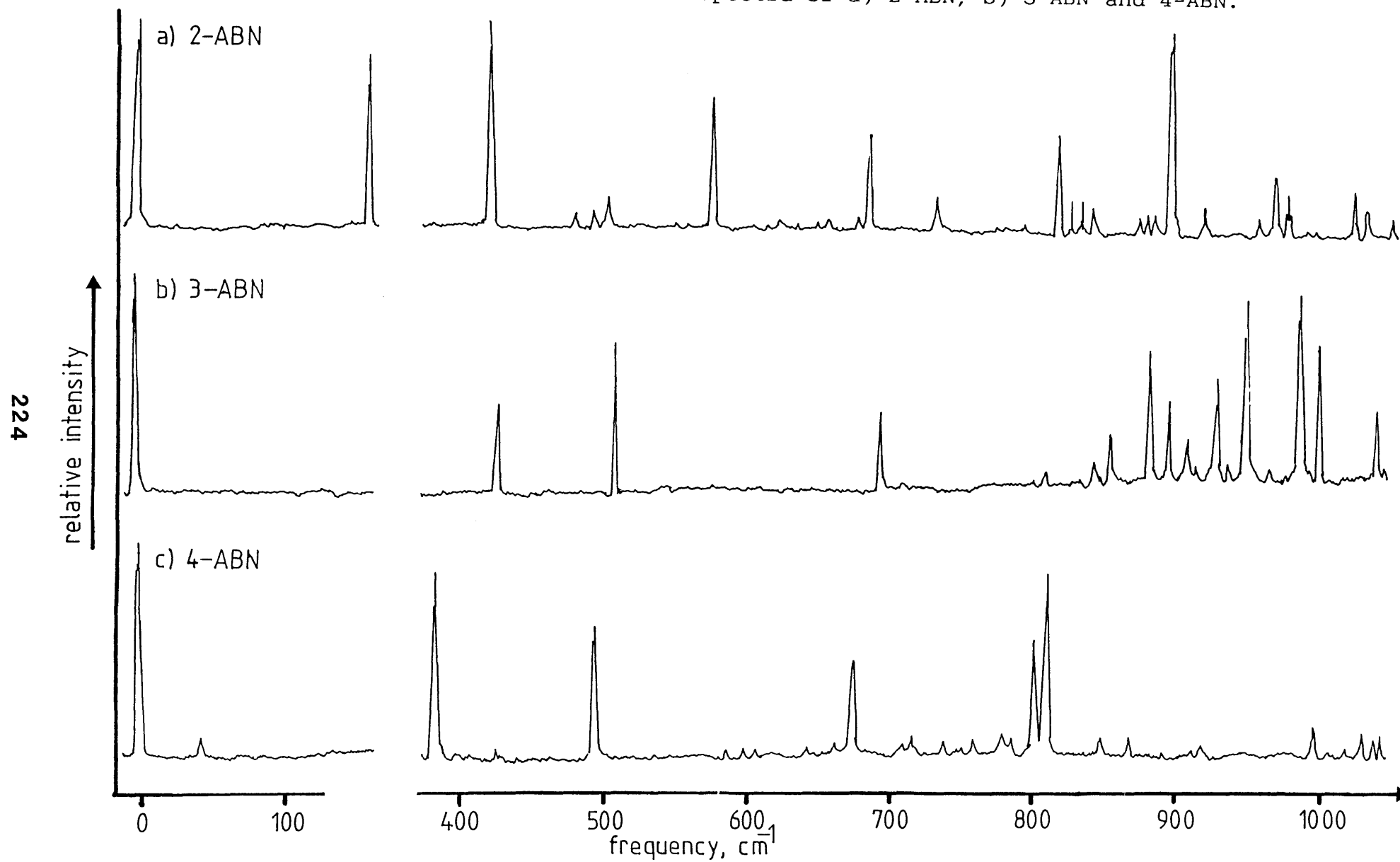


Table 5.3 Excited state assignments of the aromatic amines.

	0	6a	10b	1	12
	frequency, cm^{-1}				
Aniline ^[24]	34307	491		796	955
NMA	33302	(280)	517	774	955
DMA	32973	(218)		723	
DMABN	32333	373	494	780	
4-ABN	33493	382	492	815	678
3-ABN	31698	436		696	
2-ABN	31276	442		683	583

[25].

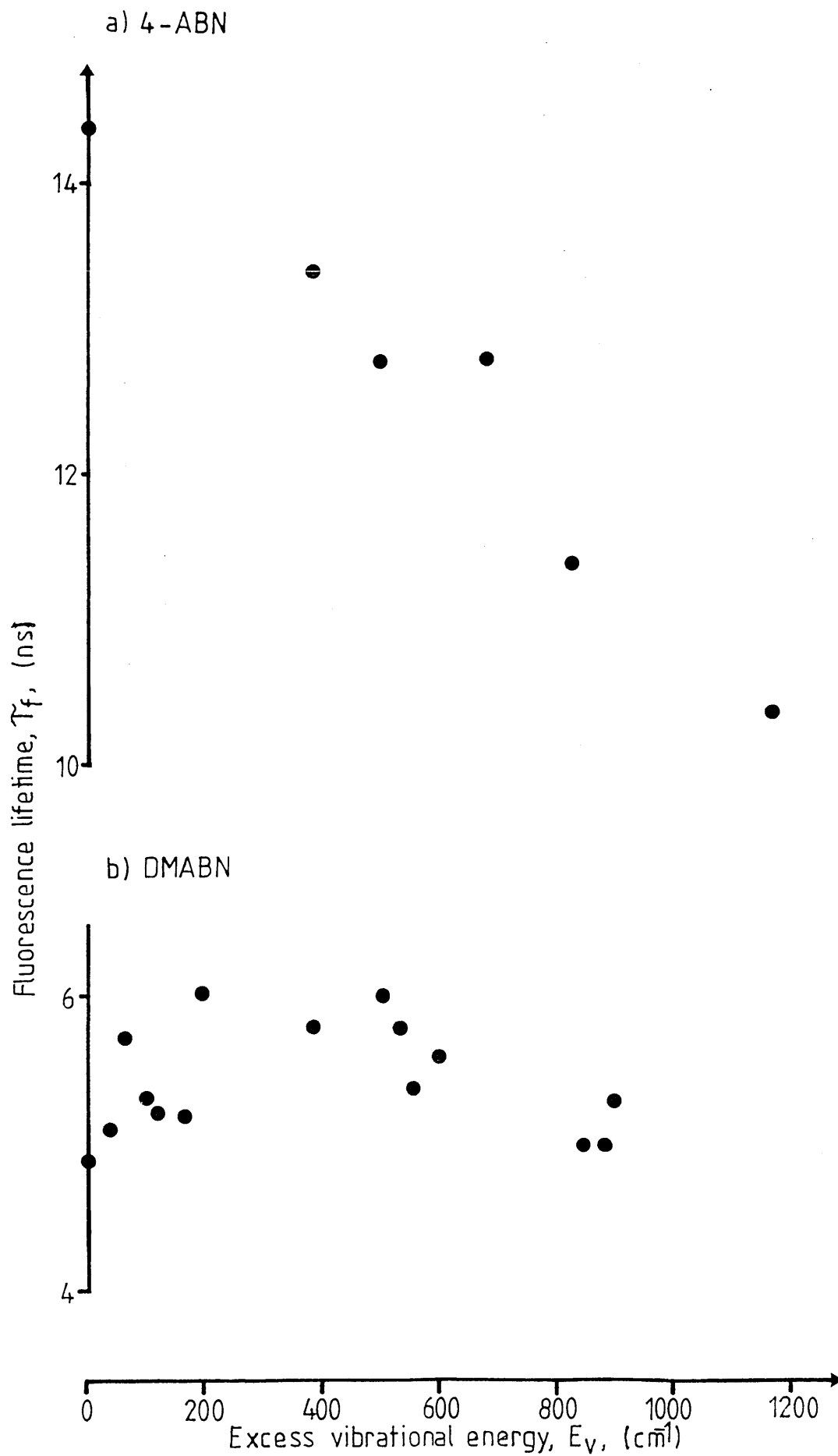
5.3.3 Fluorescence decay lifetimes of DMABN and 4-ABN

The presence of the methyl groups in DMABN appears to have a dramatic effect on the radiationless decay rate compared to 4-ABN (figure 5.4). This effect is further enhanced with DMA where the relative quantum yield appears to be reduced dramatically and the excitation spectrum becomes more complicated (figure 5.2b).

Parmenter and Stone [26] made comparisons between the dispersed fluorescence spectra of 4-difluorobenzene (4-DFB) and 4-fluorotoluene (4-FT). From their observations they deduced that the internal rotational modes of the methyl group greatly accelerated intramolecular vibrational redistribution (IVR). The dominant vibrational modes of the benzene ring were nearly coincident.

The dispersed fluorescence spectra of 4-FT (measured at 300K) revealed unstructured fluorescence present following excitation of the 410cm^{-1} mode. In 4-DFB unstructured fluorescence was not observed until the 1636cm^{-1} mode excitation. Fluorescence lifetimes, τ_f , measured for these modes were lower, though virtually unchanged with excess vibrational energy, E_v , for 4-FT, whilst those for 4-DFB were an order of magnitude greater

Figure 5.4 Plot of fluorescence lifetimes, τ_f , versus excess vibrational energy, E_v , for a) 4-ABN and b) DMABN.



and varied significantly with E_v .

It is interesting to note that despite the complicated spectrum of DMABN the main ring modes 6a, 10b and 1 vary little in frequency from those of 4-ABN in the fluorescence excitation spectra (see table 5.3). In DMABN unstructured fluorescence was observed early on (see figure 3.4) with the fluorescence being totally unresolved on excitation into the 840cm^{-1} mode. Comparison with the equivalent mode in 4-ABN (815cm^{-1}) reveals no structureless fluorescence (see figure 4.7) and indeed does not, even on excitation to 1165cm^{-1} . The fluorescence lifetimes of DMABN show little variation with E_v compared to 4-ABN (figure 5.4).

Parmenter and Stone [26] carried out the experiments at 300K and reported that when super-cooled, 4-DFB and 4-FT did not have such pronounced differences. However, the evidence presented here for DMABN and 4-ABN suggests that substitution of the amino group with two methyl groups accelerates IVR. Whether it is the methyl groups or the entire amino group which is responsible remains unclear.

Powers et al [27] made a study of the effect of alkyl chain length on the vibrational relaxation of jet-cooled alkylbenzenes. They found that for early members of the alkylbenzenes sharp unrelaxed fluorescence is observed. In the case of longer chain members a

sufficient density of states is achieved and IVR proceeds to an essentially complete randomization on a sub-nanosecond timescale. The IVR process is dominated by torsional motion about the phenyl-alkyl chain. The frequency of which is directly affected by the lengthening of the alkyl chain [27]. In aniline, the torsional modes are not active and the same is expected for 4-ABN. Though there is some weak vibrational structure in evidence to the blue of the origin. Significantly, there is a band at 42cm^{-1} which was initially thought to correspond to a torsion around the phenyl amino bond but on closer inspection this band was not repeated throughout the spectrum as in the characteristic pattern of DMABN. The explanation for sharp spectra without any unrelaxed fluorescence may be that molecules possess insufficient density of states at this level of excitation to permit any dynamical IVR process to occur on a nano-second timescale.

On complexation the observed τ_f changed little from that of the bare molecule in both 4-ABN and DMABN. This is consistent with other studies which found that excitation below the barrier for dissociation gives similar τ_f s for the complex as for the bare molecule [28,29].

5.3.4 Van der Waals complexes of 4-ABN and DMABN

The fluorescence excitation spectra of 1:1

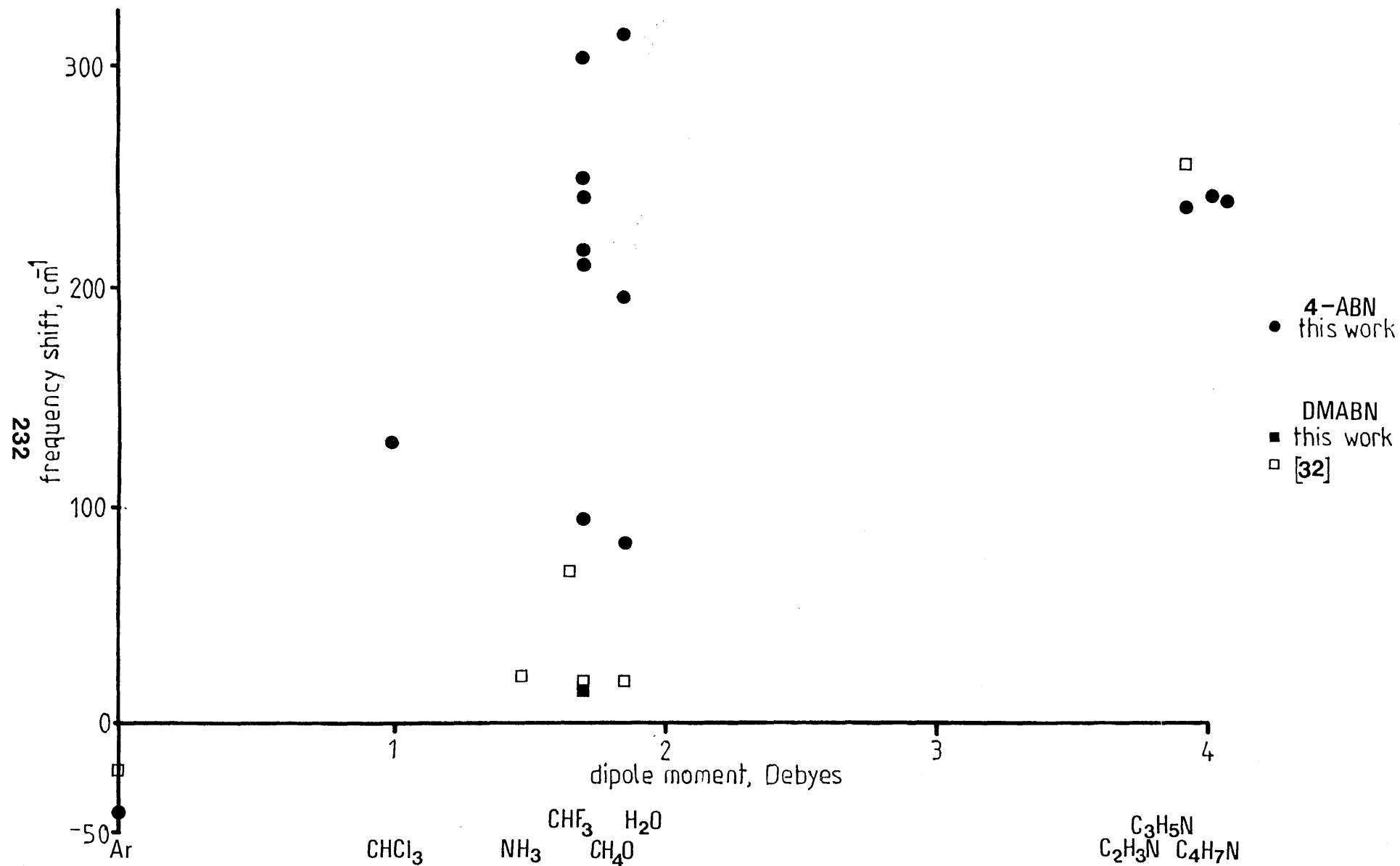
DMABN-CH₃OH (Chapter 3), DMABN-H₂O and DMABN-CF₃H [30] complexes were shifted to the blue of the bare molecule spectrum by 19, 18 and 69cm⁻¹ respectively. The complex spectra displayed the same low frequency structure as observed for the bare molecule indicating interaction of the solvent molecule with the benzonitrile moiety rather than the dimethylamino group. The hypsochromic spectral shift could be accounted for in terms of the calculated change in electron distribution on excitation, as discussed above. These complexes do not exhibit anomalous a* emission. Increasing the partial pressure of complexing agent in the expansion resulted in the formation of complexes of higher stoichiometry, as manifested by the decrease in intensity of the excitation features due to the bare molecule and 1:1 complexes. However, no new excitation features due to complexes of 1:2 (or higher) stoichiometry could be found. Kobayashi et al [30] attributed this behaviour to the possession of a small absorption coefficient by the 1:2 complexes. The interpretation given in Chapter 3 is that such complexes are non-emissive (or too weakly emissive to be observed). Time-of-flight mass spectrometry (TOFMS) would be a possible method of observing such complexes. Indeed, a recent publication was made by Warren et al [31] for TOFMS of jet-cooled DMABN/H₂O 1:1 complex two blue-shifted bands, relative to the 0₀⁰, were observed. The first at 14cm⁻¹ is comparable with this work. The second band occurred at 199cm⁻¹ and was attributed to a complex

of differing geometry to the first. Because this feature is not observed here or in other work [30,32] the complex is thought to be non-fluorescent.

Methanol, water and trifluoromethane are all protic solvents and thus expected to form hydrogen bonded complexes with DMABN. The results obtained for 4-ABN suggest that stable hydrogen bonded complexes may be formed by interaction with either the cyano group or amino nitrogen. In the case of DMABN, only 1:1 complexes with the solvent molecule bound to the cyano group appear to fluoresce, implying that interaction of a solvent molecule with the dimethylamino group results in efficient non-radiative decay. This non-radiative decay process may correspond to formation of the a^* state.

A recent publication by Peng et al studied the formation of complexes of cold isolated DMABN [32]. Their work complemented the work here and that of Kobayashi et al [30]. Two more complexes were formed with DMABN: NH_3 and CH_3CN blue-shifted by 21 and 254cm^{-1} respectively. It is interesting to note that this was not observed for the DMABN- CH_3CN complex but on obtaining the 4-ABN complexes it was decided that the blue shift for DMABN would be much further to the blue but unresolved because of the density of bands in this region of the excitation spectrum. A plot of frequency shift versus dipole moment for DMABN and 4-ABN complexes (see figure 5.5) does not reveal a linear dependence as in the

Figure 5.5 Plot of frequency shift versus dipole moment for van der Waals complexes of 4-ABN and DMABN.



case of benzonitrile complexes.

It is possible that if enough internal energy is given to the 1:1 complex charge separation will occur similar to the situation found in anthracene/DMA systems [33,34]. However, no red-shifted emission due to the a^* state was observed. Solution phase results indicate that several alcohol molecules are required to stabilise the bare electron [35,36]. It has been indicated by Robinson and coworkers [37] that for electrons and protons a water cluster of 4 ± 1 members is the effective charge acceptor.

So far, TICT state formation from cold isolated DMABN has not been observed though it has been indicated that here that the a^* state may be non-emissive under these conditions. The problem of trying to achieve a higher stoichiometry complexes is the increase in background as has been found for fluorene complexes with water [38]. This could be overcome by using a beam that enhances the formation of large clusters [32]. TICT state formation may be more favourable for other molecules such as N,N-dimethylaminopyrroles or, as has recently been shown for 4-N,N-dimethylamino-3,5-dimethylbenzonitrile [39], where TICT emission was observed from the bare molecule. This has been shown to occur in the gas phase also and does not require solvent stabilisation [40]. The fluorescence excitation spectrum of the jet-cooled molecule was shown to be broad and

unstructured much the same as found in the gas phase although no resolvable origin was seen but red shifted fluorescence was observed. These molecules are worthy of further study.

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