

SPECTROSCOPIC STUDIES
OF
PROTOTROPISM IN COMPLEX HYDROGEN BONDED CATIONS.

A thesis submitted to the University of London
for the degree of Doctor of Philosophy.

by

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JANUARY, 1978.

ABSTRACT

Formally symmetric hydrogen bonded complexes, $(B_2H)^+$ (B = a pyridine base), have been examined by various spectroscopic techniques with the object of further understanding the nature of the proton potential. The work supports the view that, in solution, the potential is polarised by local electric fields to give results characteristic of a pseudo-static asymmetric potential. Proton transfer may then occur when the polarisation changes. For symmetric potentials a mechanism is proposed in which proton transfer rates are enhanced by a lowering of the potential barrier caused by fluctuations in the N-N distance.

Examination of bands due to the internal modes of the pyridine symmetric complex at -180°C suggests that the single bands observed at room temperature are due to the proton donor moiety alone, so supporting the pulsed charge cloud model.

^1H n.m.r. measurements upon various formally symmetric complexes indicate that the formation constant and the deshielding of the bridging proton upon complexing are greater, the stronger the base. The u.v. spectrum of $(qu_2H)^+$, (qu = quinoline), has been measured by a novel method and shows some differences from the summed spectra $qu + quH^+$. The fluorescence of quH^+ is quenched dynamically by addition of free base and a hydrogen bonding mechanism is suggested.

/...

Crystals of $(3,5 \text{ dimepy}_2\text{H})^+$, (3,5 dimepy = 3,5 dimethyl pyridine) have been prepared and examined spectroscopically and crystallographically. Infra-red evidence suggests that the proton potential is asymmetric but no firm conclusions can be drawn from the crystallographic results. It is believed that this is the first such pyridine-type complex to be crystallised.

ACKNOWLEDGEMENTS

It is a pleasure to thank my supervisor, Dr. J.L. Wood, for his help and encouragement throughout the period of this research. I am indebted to Dr. D.F. Evans and to other members of the staff of this department for their helpful advice during Dr. Wood's absence. I wish to thank Dr. J. Mason of the Open University for many conversations on the various aspects of n.m.r. and Dr. T.B. Posner for her patience in running ^{15}N spectra at Milton Keynes. I am grateful to Mr. D.J. Williams of the Chemical Crystallography section for providing valuable data and advice on the crystal structure. I must acknowledge the advice of Mr. J.J. Couzens of the Imperial College Computer Centre on all aspects of computing.

Finally it is a pleasure to record the many helpful conversations with my colleagues in this department, Dr. B. Borah, Mr. S.F. Tayyari and Mr. B.P. O'Hare.

I wish to acknowledge the receipt of a studentship from the Science Research Council.

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CHAPTER 1

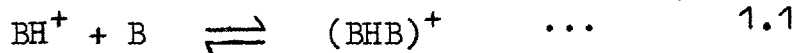
1. INTRODUCTION

1.1 The Definition of the Hydrogen Bond and Some Terms Used

There is little doubt that the hydrogen bond is one of the most comprehensively studied of natural phenomena. The enormous number of books and review articles¹ published and the immense range of techniques used bear witness to that fact. It is beyond the scope of this work to provide a comprehensive discussion of the nature of the hydrogen bond; however it is important at the beginning to define some of the terms used.

The inadequacy of any all-embracing definition of the hydrogen bond has been pointed out by Wood². His definition of a weak interaction between a strongly polar group A-H, and a strongly electronegative atom, B, in which the hydrogen atom is specifically involved, is satisfactory for general purposes. However, in the present context, in which we shall be dealing with symmetric and slightly asymmetric hydrogen bonded complexes, a second definition may be considered more appropriate. This is the interaction between two electronegative atoms in which a proton is specifically involved. This definition has the merits of not assigning proton donor and acceptor roles immediately and of not restricting the hydrogen bond to the H....B interaction of the first definition.

The hydrogen bonds of current interest are those between two nitrogen atoms in heterocyclic bases (e.g. pyridine, imidazole). Bonds are formed by the reaction of a heterocyclic base with its conjugate acid:

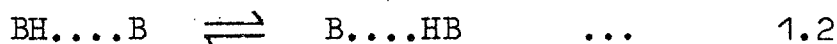


The resulting species, the hydrogen-bonded complex, cannot, except in a few cases, be crystallised; experimental observations of the complex have therefore to be made in solution.

In section 1.2 the important topic of the nature of the proton potential will be discussed. It will be shown that a double-minimum potential well is strongly indicated, implying that the instantaneous picture of the complex



is more acceptable. The use of the terms proton donor and proton acceptor in the complex refers then to the roles BH and B respectively. In the time-averaged picture the two roles are not distinguished as the proton transfer process, prototropism:



takes place rapidly. It can be seen from this that to identify only the H...B bond as the hydrogen bond is inappropriate.

The terms symmetric and asymmetric are used in this work to distinguish the two types of complex $\text{B}_1\text{H} \dots \text{B}_1$ and $\text{B}_1\text{H} \dots \text{B}_2$ respectively. The intention is not to imply anything about the instantaneous position of the proton.

1.2 The Double Minimum Potential

Much interest in studies of hydrogen bonding centres around the nature of the potential well in which the proton is located. Is it a single or double minimum potential? Is it symmetric, or asymmetric? Does it

have a high or low barrier? Of all the types of potential considered the double minimum has aroused the most interest. Indeed, in a recent book^{1b} no less than five chapters were concerned with the existence and consequences of the double minimum potential.

In the case of isolated complexes between neutral molecules, calculations³ show the presence of an asymmetric single minimum. However for complexes with overall charge (e.g. $(\text{AH}\dots\text{B})^+$) such calculations^{4,5} indicate double minimum potentials with symmetric or asymmetric potentials. A calculation⁶ for $\text{H}_3\text{N}\dots\text{HF}$ which included a six membered shell of water molecules showed a double minimum, the ion pair $\text{H}_3\text{NH}^+\dots\text{F}^-$ being stabilised by general solvent interactions.

Whilst it is known that such ab initio calculations can produce a variety of widely different answers, experimental results may be used as a basis for calculations. Vibrational spectra have provided the richest source of data and many calculations have been carried out using double minimum potentials. Treatments have generally been limited to those in which, (1) the A-B distance is fixed and the A-H stretch is considered⁷ or (2) coupling between the A-B stretch and either the A-H stretching⁸ or A-H bending⁹ mode is allowed in a two-dimensional model. Both linear and bent bonds and symmetric and asymmetric potentials have been treated. Most common potential functions are polynomial¹⁰ although those based upon the Morse curve have also been applied¹¹.

In a comprehensive review of the vibrational spectra of hydrogen-bonded complexes, Wood² has discussed

a number of phenomena which may affect the spectra, including the double minimum potential. That a double minimum potential exists in some of the hydrogen bonds under consideration in this work has been established by elimination of the alternatives¹². Two problems remain outstanding. The first is an explanation of the fact that some observations cannot be reconciled with the double minimum potential model. The second is a more detailed study of the behaviour of the proton in the double minimum potential and the evaluation of the well dimensions.

1.3 Tunnelling

If a proton is located in a double minimum potential then it may exhibit the quantum mechanical effect of tunnelling through the potential barrier. Whilst classical mechanics allows a particle to cross a potential barrier only if its energy is greater than, or equal to, that of the barrier, quantum mechanics allows a finite probability that the particle may pass through the barrier with an energy less than that at the top of the barrier. This effect is termed tunnelling. There is also a finite probability that a particle with energy greater than that of the barrier may be reflected.

This phenomenon may be explained by recourse to the particle/wave duality concept, commonly applied to the photon and electron. Zimmermann¹³ has coined the phrase protonic state to describe the quantisation of energy of the wave proton in a potential well.

Wave functions for a proton in a parabolic potential well are shown in figure 1.1. They are obtained

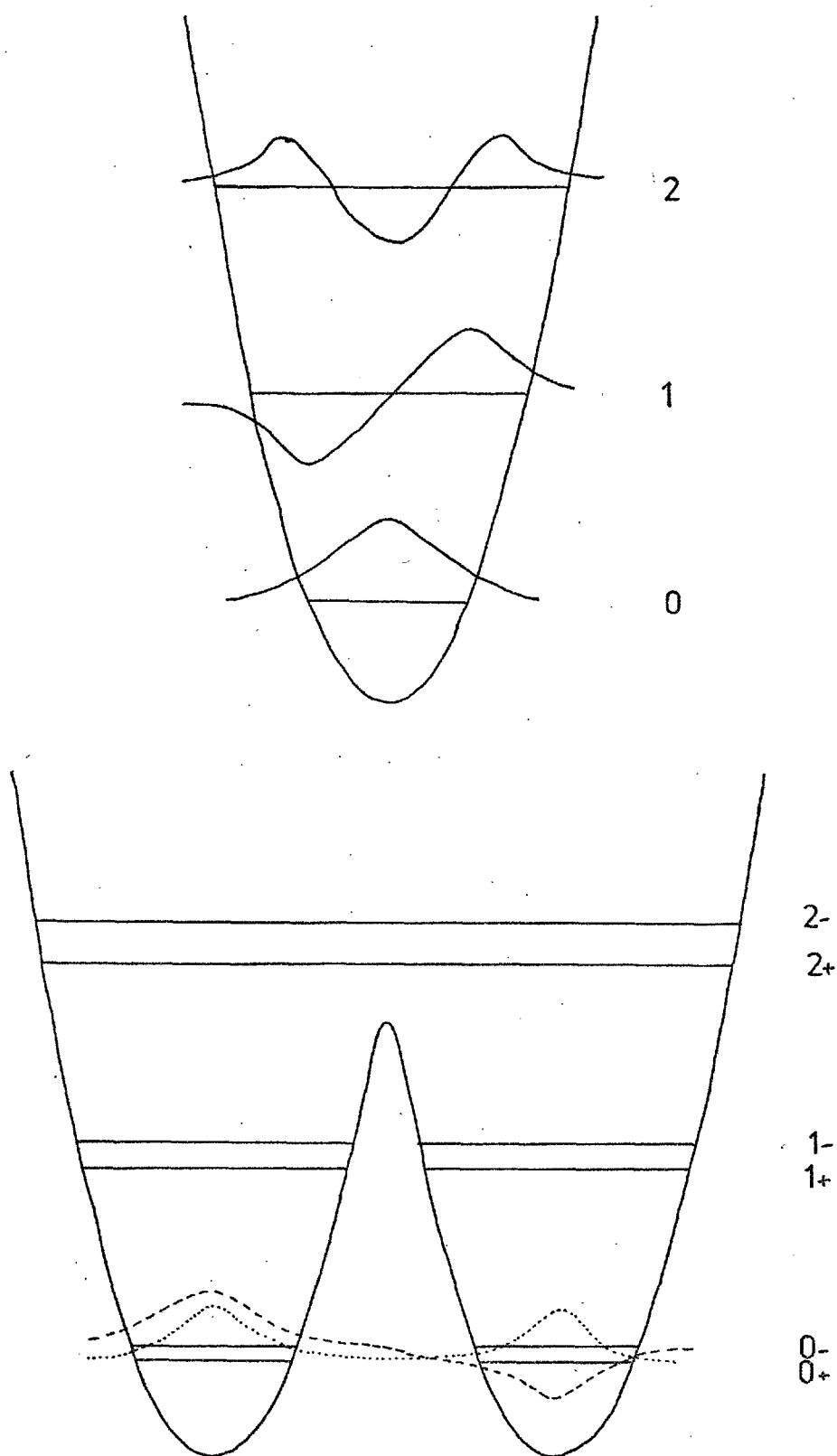


Figure 1.1 (a) Proton wave-functions in a harmonic oscillator.
 (b) Proton wave-functions in a double minimum potential formed from two intersecting harmonic oscillators.

by solution of the harmonic oscillator wave equation. It can be seen that the functions penetrate the potential walls. If two equal parabolic wells intersect, then overlapping of degenerate protonic states can occur, depending upon the thickness and height of the barrier. For a symmetric double minimum potential this overlapping gives rise to symmetric and antisymmetric functions. The splitting of the energy levels increases towards the top of the barrier and is a measure of the rate of proton transfer. Prototropism also increases with a lower or narrower barrier.

Substitution of deuterium for hydrogen in the bond reduces the tunnelling rate considerably, since deuterium has twice the mass and hence half the de Broglie wavelength. This reduces the overlap between wells. In addition the zero-point-energy for the deuteron is lower than that for the proton. Experimental comparison of protonated and deuterated systems can often supply evidence of tunnelling although the results must be treated with caution since other effects may contribute to observed differences.

The effect of asymmetry in the potential function has been demonstrated¹⁰. The protonic state wavefunctions become localised and the degree of overlap is considerably reduced, slowing the tunnelling rate.

The importance of tunnelling in proton transfer reactions has been stressed^{14,15}. Formation of hydrogen bonds¹⁶ prior to proton transfer is most likely. The proton may then cross the barrier by classical or quantum mechanical means, depending upon the conditions. A wide

range of conditions can be studied, however it seems that the predominating effect may be the fluctuation in the A-B distance which will be discussed later. The effect of such fluctuation is to blur out the protonic levels making tunnelling more likely.

Classical proton transfer over the barrier will take place if the barrier is too wide or high for the tunnelling rate to be appreciable. It is important, however, to realise that both processes cannot be considered simultaneously in the same system. If a net transition rate from a number of protonic states is to be considered, then the individual rates may be summed using the appropriate partition factor for each state.

1.4 The Role of the Environment

For hydrogen bonded species in solution, the consideration of the system in isolation is clearly unrealistic. Qualitative inclusion of the environment in quantum mechanical calculations makes them considerably more complex¹⁷ and cannot be carried out without many assumptions. A review by Weidemann¹⁸ considers correlations between proton transfer in the hydrogen bond and both other hydrogen bonds and the solvent/counter-ion environment. An important consequence of these correlations is that the double minimum is now a function of some environmental coordinate. One solution to this problem is to separate the motion of the proton from the environment. This can only be valid in cases where the proton tunnels at a much faster rate than that of the rearrangement of the environment. In this case, then,

double minimum potentials may be drawn and proton transfer may be considered for the instantaneous picture of the hydrogen-bond in each environmental situation.

The high polarisability of symmetric hydrogen bonds has been discussed by Janoschek et al ¹⁹. It is a consequence of the sensitivity of the proton distribution in the double minimum potential to a small degree of asymmetry which may be caused by local field gradients. It is shown that such polarisability should be strongest where the barrier height is greatest and hence the longer the hydrogen bond the greater the polarisability. NH...N systems are therefore expected to exhibit greater polarisability than those of OH...O ²⁰.

Borah and Wood²¹ have used this theory of polarisability to explain observations on the symmetric complex, $(bz_2H)^+$ (bz = benzimidazole), in the infrared spectrum. They show (figure 1.2) some suggested one-dimensional asymmetric potentials which, when combined with an environmental function, give a symmetric function. Use of such an environmental function implies that the infrared spectrum of the complex should be strongly sensitive to a change in solvent or counter-ion. Although this environmental solution has been invoked to explain observations in a series of complexes of heterocyclic bases¹², only a few systems have exhibited behaviour totally in accordance with the suggested theory.

Environmental explanations for various kinetic observations have been proposed²². Steric hindrance to close approach of solvent molecules allows a faster proton transfer rate.

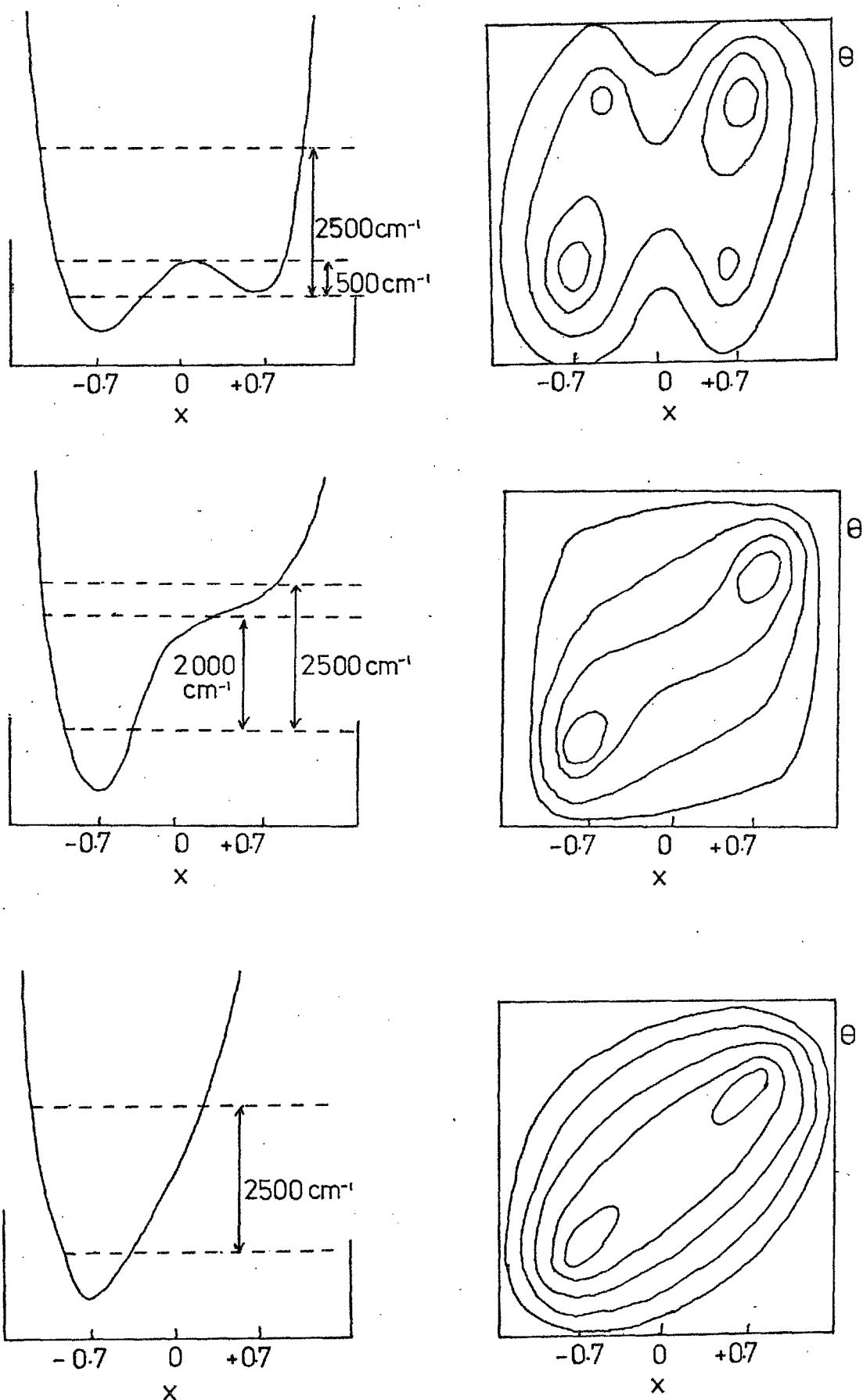


Figure 1.2. Some possible asymmetric potential wells, (a)-(c), representing sections through the two dimensional energy contours, (d)-(f), for constant θ , the environmental configuration coordinate.

The restriction caused by the insolubility in many solvents of the salts BH^+X^- has led to the general use of only the free base or acetonitrile as solvents. Acetonitrile is a weak proton acceptor but does not act as a proton donor²³. It therefore enhances the basicity of most bases (the pK_a of a typical amine in acetonitrile is between 7 and 8 points higher than in water) and most strongly reduces the acidity of most acids. For this reason the study of acid-base chemistry in acetonitrile includes the stabilisation of ions by homo-conjugation; in other words the formation of conjugate acid-base hydrogen bonds (i.e. reaction 1.1).

1.5 The significance of prototropism in biochemistry

The extreme importance of hydrogen bonding in biochemistry is well known. Stabilisation of proteins with a secondary molecular structure²⁴ is an important example.

The function of deoxyribonucleic acid (D.N.A.) in carrying the genetic code is well known. Replication occurs²⁵ by the breaking and reforming of multiple hydrogen-bonded base pairs (figure 1.3). A mechanism in which breakage takes place after proton transfer to give different bases has been proposed by Löwdin²⁶. These errors in the genetic code may be reproduced and multiplied, causing mutation and the development of tumours. Shulman²⁷ has suggested that experimental evidence indicates a double minimum potential in the adenine-thymine base pair.

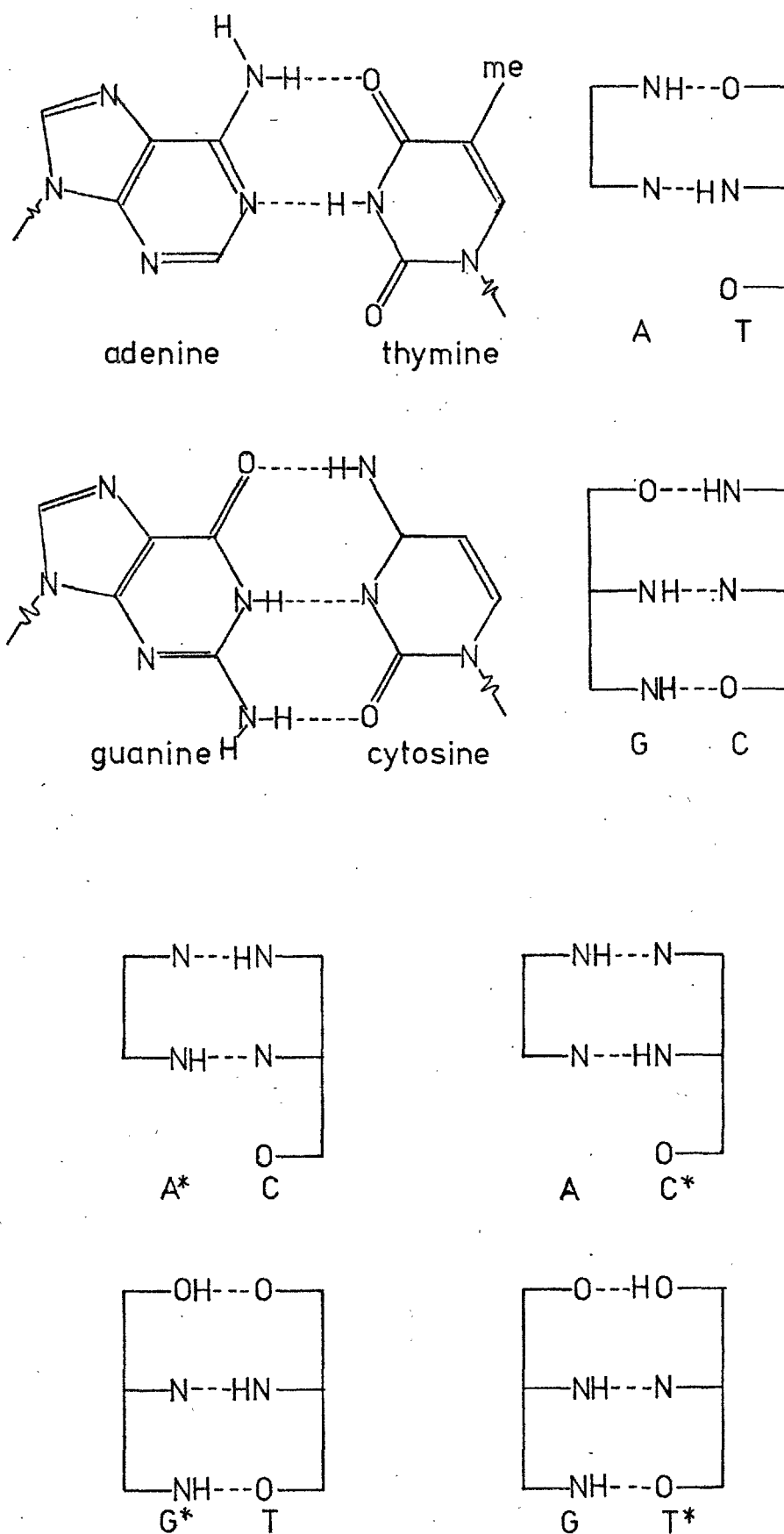


Figure 1.3. (a) The complementary base pairs of D.N.A.
 (b) Schematic representation of the mismatched D.N.A. base pairs.

1.6 Methods of Investigation of Hydrogen bonds

A great deal of evidence has been amassed for the existence of hydrogen bonds in many systems. Prime among these may be cited the striking differences² in the A-H stretching mode between the free proton donor and the hydrogen-bonded complex. This section only deals with those methods of investigation that have some importance in the present study. Many reviews and books^{1,2} provide a more complete exposition and interpretation.

1.6.1 The Infra-red and Raman Spectra

If the participants in a hydrogen bond are polyatomic, bond formation may have a marked effect upon their internal vibrations²⁸. Frequencies may be shifted and bands broadened. The theoretical relationship between the nature of the proton potential function and the internal modes has been treated extensively²⁹. Theory predicts a splitting of each band into a quadruplet due to tunnelling through the double minimum potential and coupling of the internal mode with the A-H stretching mode (Figure 1.4). In the absence of coupling, only two transitions are allowed - the splitting is 2Δ (Δ is the tunnelling frequency). Coupling has the effect of enlarging the splitting in the excited states of the internal mode and allowing all transitions.

Figure 1.5 shows the potentials and the predicted positions of the peaks for one internal mode, for symmetric and asymmetric potentials. The expected intensities of the individual peaks are shown; there is no indication of individual band-widths but it is to be expected

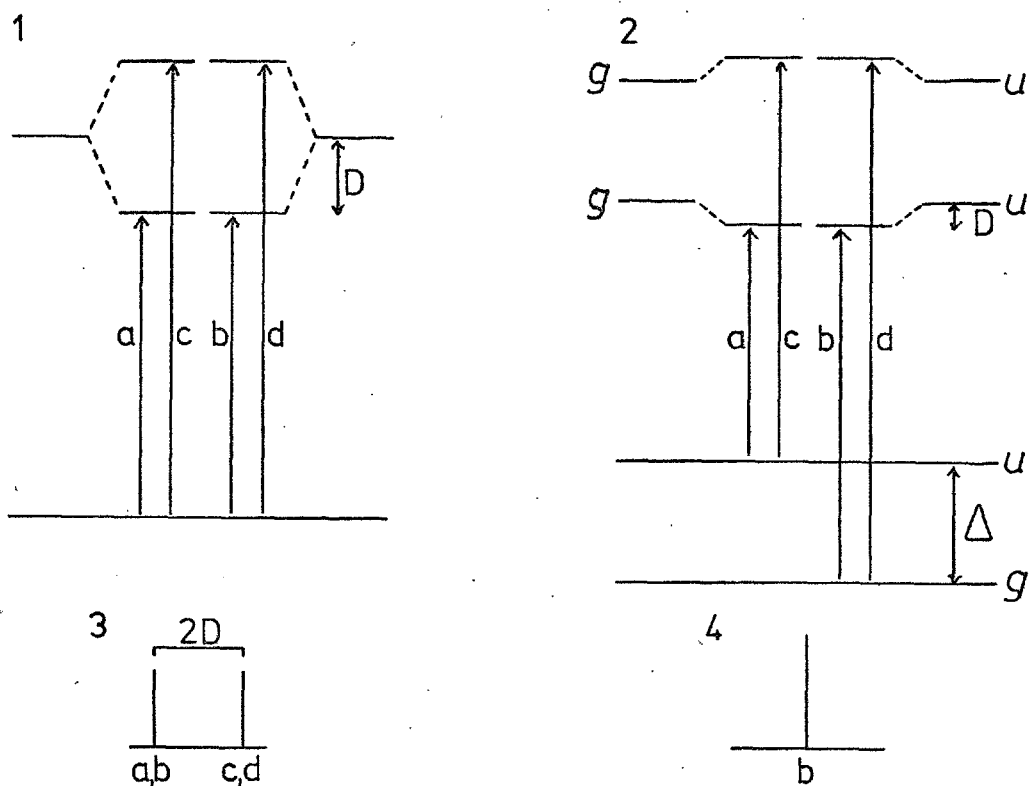


Figure 1.4.

Energy levels of the ground state and first excited state of a pyridine internal mode with (1) no tunnelling (high barrier double minimum potential) and (2) fast tunnelling. a , b and c , d are transitions characteristic of the proton donor and acceptor (or vice versa) respectively. When tunnelling occurs the levels are further split. (3) and (4) show the corresponding model spectra. In (4) only transition b is intense enough to be observed. This model assumes an isolated symmetric complex.

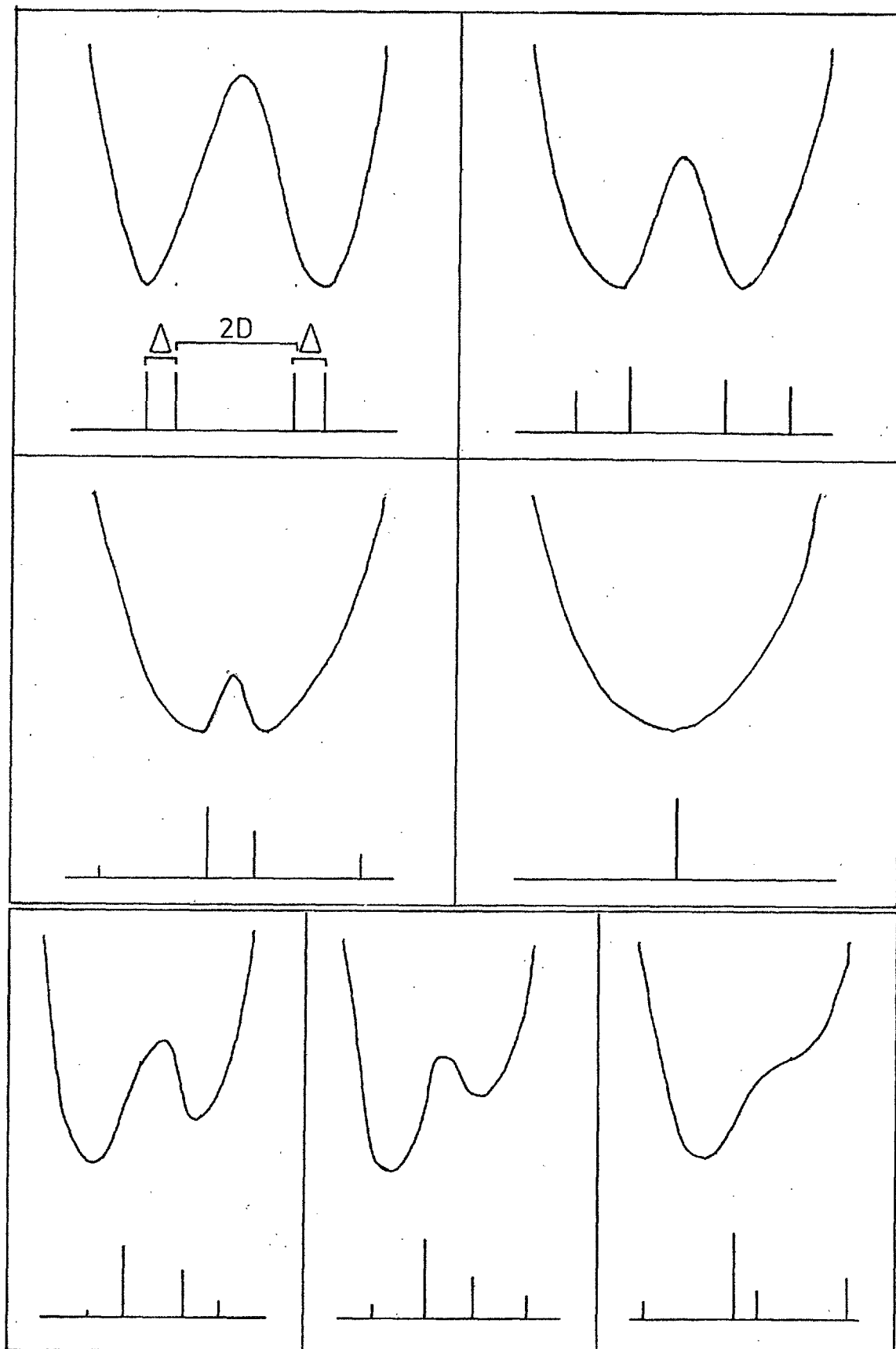


Figure 1.5. The effect of various proton potentials upon the appearance of an internal mode. (Reference 29) The variation in the appearance is due to an increase in the tunnelling frequency and a decrease in the coupling term from a - d.

that substantial overlapping of the bands will occur. Thus the observation of one peak may indicate either splitting by tunnelling, in the absence of coupling with the A-H stretching mode, or splitting by $(2D + \Delta)$ due to the coupling. It is to be expected that, for different internal modes, whilst Δ remains constant, D will vary. In the absence of the coupling term, the two peaks observed should be characteristic of the proton donor and acceptor moieties.

Evidence for the double minimum potential in symmetric complexes from infra-red studies on the modes most intimately connected with the hydrogen bond is so strong¹² that the failure to observe doubling or abnormal band-shapes in the internal modes is surprising. Proposed explanations are that only one peak is strong enough to be observed or that the splitting is extremely small resulting in a marginal broadening of the natural peak width. One aim of the present work is to provide an explanation for the incompatibility of the ring mode evidence with the double minimum potential.

1.6.2 Diffraction studies

Both X-ray and neutron diffraction studies have proved most useful in the examination of hydrogen bonds in solids. A comprehensive text by Hamilton and Ibers³⁰ provides an excellent introduction to these studies.

Whilst the location of hydrogen by X-ray diffraction is notoriously difficult because of its low scattering factor, evaluation of the A-B distance has frequently been used to identify hydrogen bonds, since it is commonly

less than the sum of the van der Waals covalent radii for A and B. Neutron diffraction can be used where location of the proton is required. In a recent study³¹, the permanently asymmetric location of the proton in the complex, $(bz_2H)^+$ (bz = benzimidazole), was inferred from the different dimensions of the rings on either side of the hydrogen bond.

1.6.3 Electronic spectra

The effect of hydrogen bonding upon electronic absorption spectra is often small and frequently indistinguishable from general solvent effects. The effect of proton transfer upon spectra is, however, often dramatic, since the position and intensity of peaks due to ions are generally different to those of their conjugate acids and bases. The strength of an acid or base is frequently greater in a $(\pi^* \pi)$ state than in the ground state, although a base will be weaker in a $(\pi^* n)$ state.

The role of the Franck-Condon effect in the frequency shift upon hydrogen bonding has been discussed³². If the complex is more stable with respect to dissociation in the excited state than in the ground state, (as implied in $\pi^* \leftarrow \pi$ transitions) a red shift is to be expected upon complexing. Conversely, if the complex is less stable in the excited state ($\pi^* \leftarrow n$ transitions) a blue shift should be observed. A correction, due to the Franck-Condon effect, prevents direct measurement of the change in hydrogen bond energy (figure 1.6).

Studies³³ of prototropic equilibria by u.v. absorption spectrophotometry suggest that for uncharged

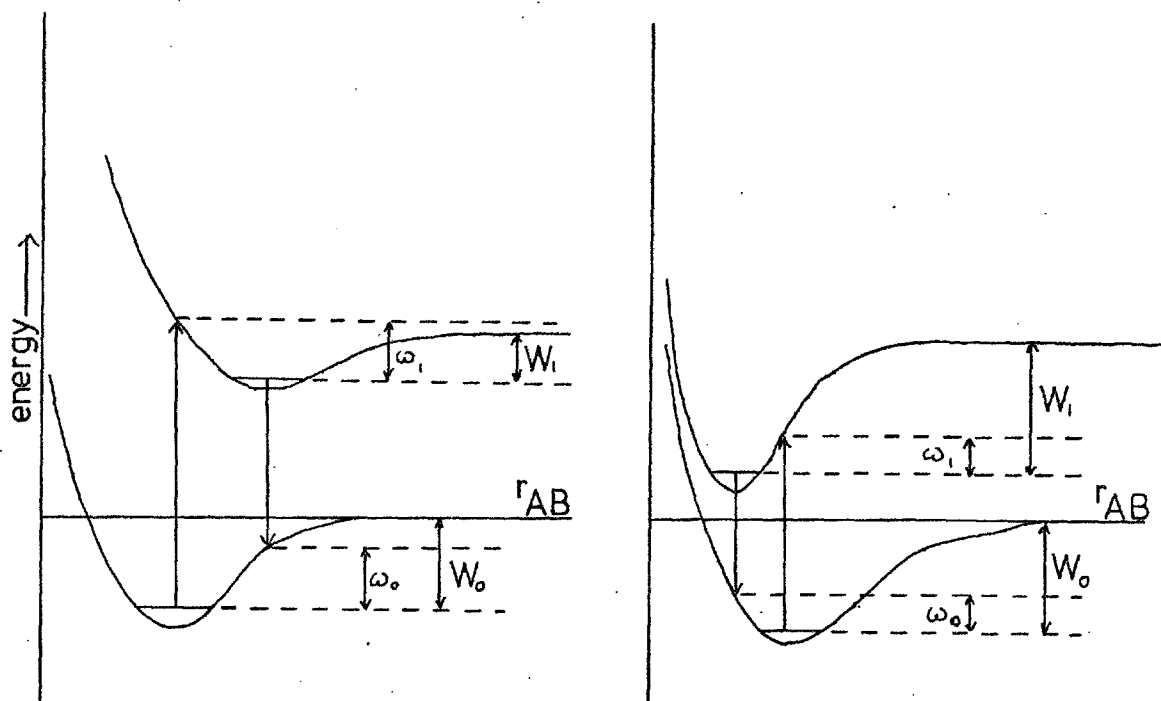
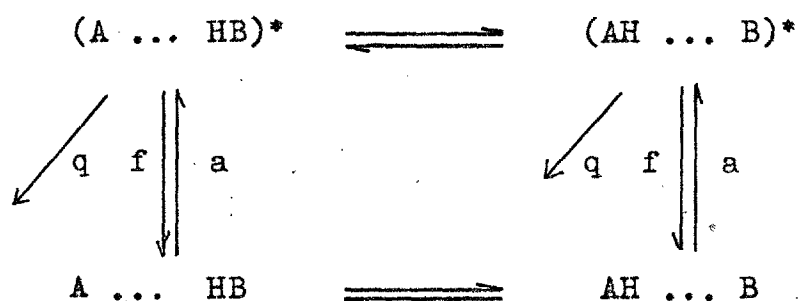


Figure 1.6.

The role of the Franck-Condon principle in hydrogen bonding (a) shows a hydrogen bond which is less stable in the excited state than in the ground state; (b) shows the converse situation.

Figure 1.7.



Electronic excitation as a prelude to prototropism.

complexes, AHB, there should be a range of solvent polarities of dielectric constant environments in which the hydrogen bonded ion pair, $A^{\cdot-} \cdots HB^+$, is more stable than the normal complex, $AH \cdots B$. Evidence for such ion pairs is tenuous since it relies on the observation of bands characteristic of the ions. If a double minimum potential is accepted then the presence of hydrogen bonded ion-pairs is certain. But if the potential has an asymmetric single minimum then the ion pairs will be unstable with respect to the free ions.

Fluorescence spectrophotometry has proved a powerful tool in the study of hydrogen bonding in excited states. The changes in acid and base strength upon excitation imply a change in the proton potential and a possible reversal of the roles of proton donor and acceptor. Thus a reaction scheme of the type indicated in figure 1.7 may be envisaged. Electronic excitation can be a prelude to proton transfer in the excited state and following fluorescence, proton transfer in the ground state. The time-scale of fluorescence decay in certain systems may be competitive with proton transfer processes³⁴.

Mataga and co-workers have observed fluorescence quenching of naphthols and naphthylamines by pyridine³⁵ and of acridines by phenol³⁶. Both have been explained in terms of the interaction of the π -systems of the two molecules through a hydrogen-bond. In systems where only one moiety is aromatic, a shift in the frequency of fluorescence is observed. In the case of β -naphthol-triethylamine, the characteristic naphthol fluorescence is replaced by that of conjugate base³⁷. The effect is solvent

sensitive³⁸ indicating that proton transfer to a hydrogen bonded ion pair takes place in more polar solvents. An anomalously large effect in acetonitrile has been interpreted as being due to ionic dissociation. These observations are all interpreted in terms of photochemical prototropism, during the lifetime of the excited state, however measurement of the rate of proton transfer does not appear to have been achieved. The study of hydrogen bonding in excited states is being advanced extremely fast at present and it seems that such studies may lead to useful comparisons with ground state systems.

Another promising line of attack is that of time resolved fluorescence experiments³⁹ in which the prospect of obtaining a proton transfer rate may be closer⁴⁰.

1.6.4 Nuclear Magnetic Resonance

The application of proton magnetic resonance (p.m.r.) to hydrogen bonding has been reviewed by Davis and Deb⁴¹ and by Hofacker and Hofacker⁴². A discussion of the use of p.m.r. is reserved for Chapter 2.

A limited amount of n.m.r. with other nuclei has been carried out. The general rule is that upon hydrogen bonding the resonance of an atom in the donor shifts downfield and that in the acceptor shifts upfield, indicating a transfer of electron density from the donor to the acceptor. Of particular relevance here is the work of Saito and Nukada⁴³ on ^{14}N by double resonance. The shift of the ^{14}N nuclear resonance was shown to correlate with that of the bridging proton.

1.7 The Time-scale of Prototropism

Results of empirical calculations with data derived from the infra-red spectrum suggest that, in the symmetric complexes under present consideration, the rate of prototropism by tunnelling is in the region of 10^{12} s^{-1} . However the rate is extremely sensitive to the barrier dimensions and this estimate is derived from a static double minimum potential with no environmental coupling. Thus we may expect the rate to be considerably slower if the environmental coupling is strong and much faster if the tunnelling is by N-N fluctuations (Chapter 7).

The time-scale for observations in the infra-red is 10^{-13} s . Infra-red evidence which indicates the asymmetric location of the proton in symmetric hydrogen bonds therefore suggests a low life-time limit for the proton in one well of 10^{-13} s , which corresponds to a tunnelling rate of 10^{13} s^{-1} .

Failure to resolve the internal modes in some complexes raises this low life-time limit. If the instrumental resolution is of the order of 3 cm^{-1} , this gives a life-time not less than 10^{-11} s . For those complexes in which internal modes have been resolved into donor and acceptor roles^{12,21,44} the splitting is about 10 cm^{-1} - a life-time of $3 \times 10^{-12} \text{ s}$.

The time-scale of p.m.r. is dependent upon the difference in resonance frequencies of the proton at the two environments between which exchange occurs. In the case of prototropism across a symmetrical hydrogen bond, this difference is zero and no evidence is to be expected.

P.m.r. does provide evidence that proton transfer occurs, at a rate much greater than 70 Hz. This is the frequency of coupling between the ^{14}N quadrupole and the N-H proton in the pyridinium ion⁴⁵. In conditions under which complexing occurs the N-H proton gives rise to a single sharp line. If the rate of N-H bond breaking were in the region of 70 Hz or slower we should expect to see a triplet, due to the ^{14}N -H coupling. N-H bond breaking requires proton transfer, and since that to another base molecule is most likely, the hydrogen bonded complex will be the intermediary. This mechanism does not necessarily require the presence of a double minimum potential, but since such a potential is postulated the relevant exchange process is tunnelling between the two minima. This lower limit is unlikely to be helpful for the reason that it is several orders of magnitude lower than the rate for most non-tunnelling proton transfer reactions controlled by diffusion.

The faster ($\sim 10^{-15}$ s) methods of electronic spectroscopy might be expected to aid in the determination of a rate value, particularly the time resolved methods. The rate of fluorescence emission varies over a wide range in different systems so that it seems probable that some system could be found in which competition between the two processes might aid evaluation of a rate for prototropism.

CHAPTER 2

2. PROTON MAGNETIC RESONANCE STUDIES OF SYMMETRIC SYSTEMS

2.1 Introduction

Proton Magnetic Resonance (p.m.r.) has played an important role in the study of H-bonds. Bond formation generally has only a weak effect upon the resonance of the protons not involved in the bond. Naturally it is the H-bond proton which has aroused most interest and studies of this proton resonance can be divided into three areas:-

(1) The absolute chemical shift and the change in shift from the free proton donor to the complex⁴².

(2) Evaluation of equilibrium constants using the averaging of resonance positions as a measure of concentration⁴¹.

(3) Rate data, derived from line broadening measurements, for proton exchange⁴⁶.

In this section the chemical shift of the bridging proton and association constant are obtained for a variety of symmetric complexes. The results are discussed in terms of the strength of the hydrogen bond. The possibility of deriving rate data from p.m.r. is considered.

2.2 Proton Magnetic Resonance and Hydrogen Bonds

The chemical shift of a bridging proton moves to lower field upon H-bond formation unless the acceptor is a π -electron system, in which case the change is up-field. The downfield movement is associated with a reduction in the electron density around the proton. Although intuition suggests that electron density should

increase upon H-bonding, a reduction is entirely in accordance with theoretical calculations⁴⁷. The principal causes of this effect appear to be⁴² (a) magnetic anisotropy in the proton acceptor and (b) polarisation of the A-H bond by the acceptor. The effect of (a) may be to shift the resonance either up or down field and is most important where the acceptor is a π -system, in which case it causes the upfield movement. The electron distribution about the proton is deformed by (b) which causes a downfield movement.

Since the amount of polarisation might be expected to increase with shorter and stronger H-bonds, it is possible that the downfield change in chemical shift can be used as a measure of H-bond strength. Indeed a number of different measures of H-bond strength⁴⁸ (acid strength of donor, enthalpy of formation of complex and shift in A-H stretching frequency) have been shown to correlate satisfactorily with the change in chemical shift.

The effect of temperature upon the chemical shift of the bridging proton has been discussed by Muller and Reiter⁴⁹. Previously the observed downfield movement with decreasing temperature had been explained by reference to the increasing equilibrium constant for complex formation. Muller and Reiter showed that the effect was greater than that expected and was therefore a real decrease in electron density at lower temperatures. Their explanation is that the A-B stretching vibration is of such low frequency that the population of excited states is very sensitive to temperature. As the sample is cooled these

excited states become depopulated and the mean amplitude of vibrations is reduced. The bridging proton then spends a greater proportion of its time in the less electron rich centre of the hydrogen bond.

2.3 The effects of exchange upon the p.m.r. spectrum

There are few H-bonded complexes which do not undergo frequent dissociation and association in solution. The consequent exchange of the bridging-proton's environment between the complex and free donor has a marked effect upon the p.m.r. spectrum. It is useful, therefore, at this stage to discuss the effects of exchange.

For intermolecular proton transfers in which the resonance frequencies of the proton in the two different environments are widely spaced, the appearance of the p.m.r. spectrum depends upon the relationship between the frequency of the spacing and the rate of exchange. Figure 2.1 illustrates the effect. In the limit of slow exchange when the rate is much lower than the spacing, two lines may be observed, each corresponding to one of the two environments. As the rate of exchange increases, the two peaks broaden and coalesce. In the limit of fast exchange a single sharp line may be seen at a position at an average of the two individual resonances related to the proportion of the lifetime spent in each location. In addition, the splitting of the resonance peak by coupling of the proton spin with those of adjacent nuclei can be reduced or removed in much the same way.

Generally intermolecular proton transfer rates are much greater than the spacing between the lines.

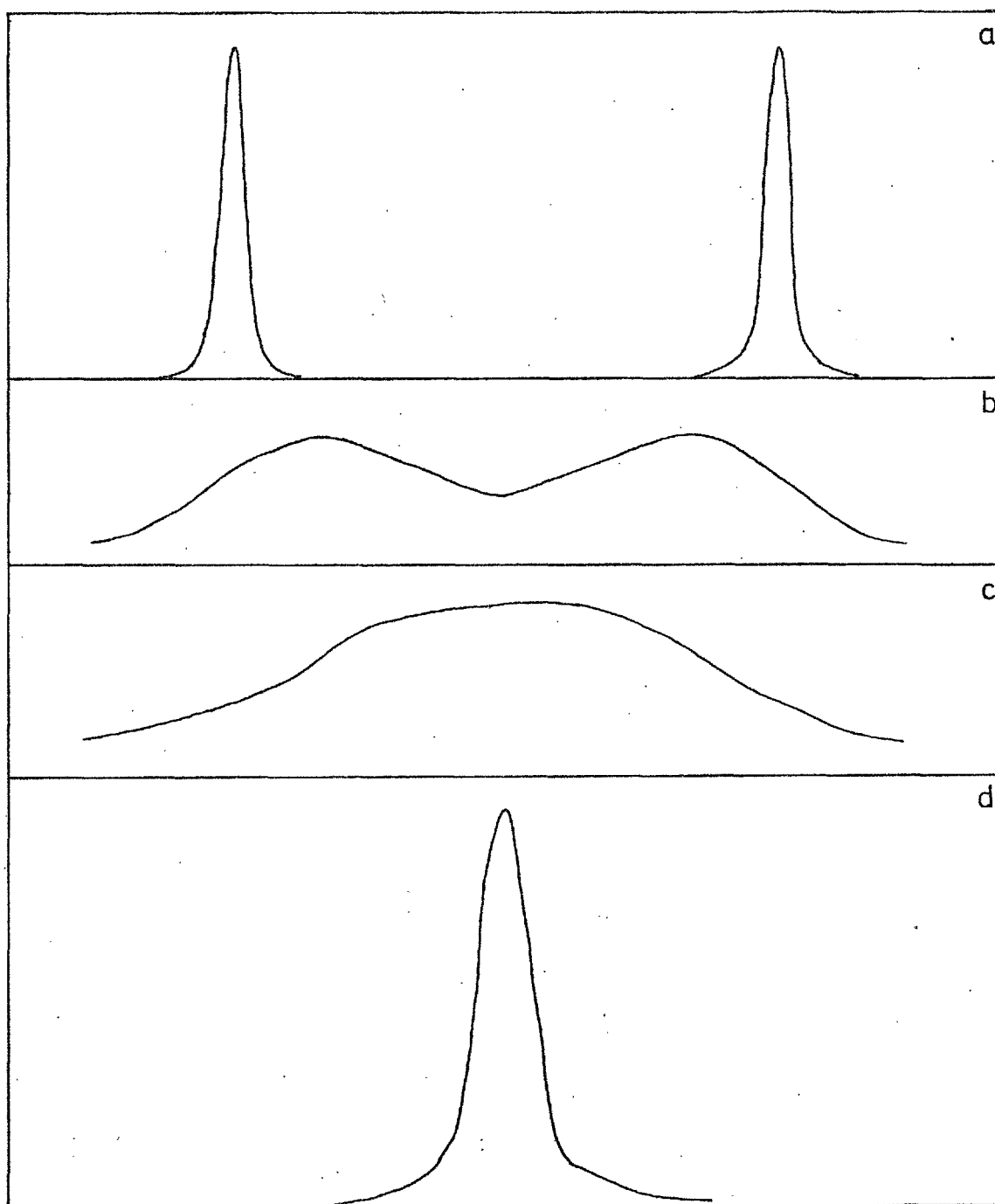


FIGURE 2.1

Proton spectra of a nucleus exchanging between two equally populated sites. The exchange rate increases in the sequence a-d. Each spectrum should have the same integral value.

For this reason most kinetic studies depend upon band width analysis and relaxation time measurement on the single band. A comprehensive review by Grunwald and Ralph⁴⁶ describes much of the work on dynamic nuclear magnetic resonance in protic solvents of nitrogen bases and their conjugate acids.

The methods of dynamic n.m.r. depend upon the concentration and pH dependence of the band width and relaxation time of the exchanging proton's resonance. From this data lifetimes and rate expressions may be derived. Results obtained are generally in good agreement with those from temperature-jump and stopped-flow techniques.

It is perhaps surprising, given the well-established nature of the technique, that dynamic n.m.r. has not been applied to proton transfer reactions in aprotic solvents. The formally symmetric systems in the present study provide a more complicated situation than those in protic studies discussed by Grunwald and Ralph. In aqueous solutions it appears that transfer occurs through a Grotthus-chain mechanism using water as an intermediate, and that the donor and acceptor do not come into direct contact. Thus the presence of only three species (B , AH and H_2O) need be considered. In aprotic solvents the effect of counterions, complexes with comparatively long life-times and, perhaps, protonated solvents is far more important.

2.4 The Effect of the ^{14}N nucleus upon the p.m.r. spectrum

Particular problems are encountered in dealing with protons directly bound to ^{14}N ⁵⁰. Apart from the characteristic lability of such protons, the presence of the ^{14}N nuclear quadrupole can severely affect the proton spectrum. This disturbance is due to the relaxation rate of the ^{14}N nuclear quadrupole, which increases with the asymmetry of the environment and depends also upon the characteristic reorientation rate of the molecule in solution.

Figure 2.2 shows the effect of the ^{14}N nucleus upon the spectrum of the N-H proton. In figure 2.2a the ^{14}N relaxation is slow compared to the ^{14}N - ^1H coupling constant (e.g. in an acidified ammonium solution). Coupling to ^{14}N (which has $I = 1$) causes the triplet. Less symmetrical environments (e.g. dry ammonia) give rise to faster relaxation rates and broadened N-H proton peaks. As relaxation speeds up still further, the triplet collapses to a broad singlet (when the coupling frequency between the proton and the nitrogen is comparable with the relaxation rate), and the peak ultimately becomes a sharp singlet at the limit of fast relaxation. Relaxation is also a function of temperature⁵¹ and of the viscosity of the solution, depending as it does upon molecular reorientation.

The effect of quadrupolar relaxation broadening may be removed by double resonance⁴⁵ at the ^{14}N resonance frequency. Under double resonance conditions the ^{14}N nucleus is rapidly exchanged between its three quantum states; the lifetime in any one state is not sufficient for coupling to the proton to be observed. In this case

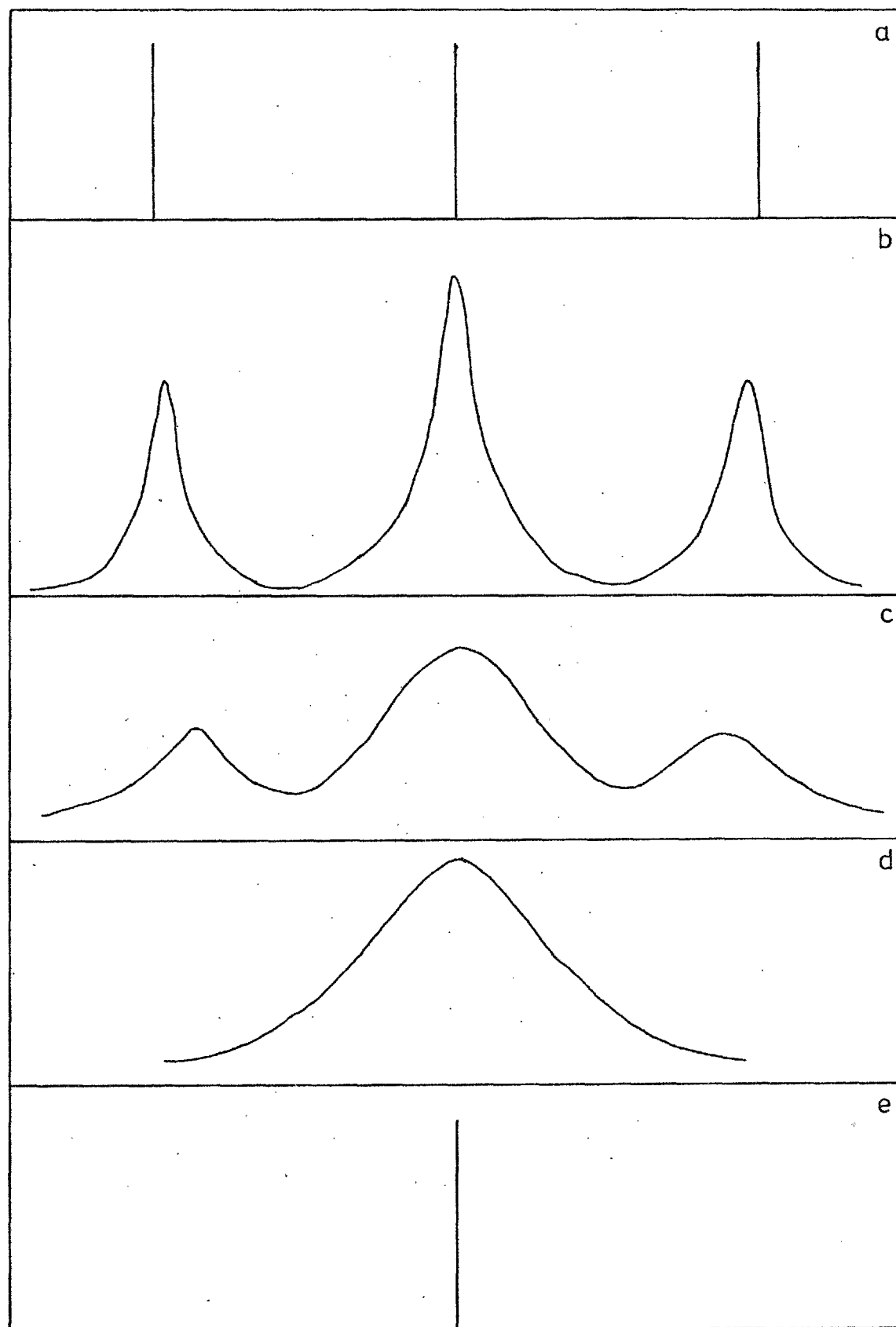


FIGURE 2.2

Proton spectra of a molecule containing a proton coupled to a ^{14}N nucleus showing the effect of an increasing quadrupolar relaxation rate (a to e).

a single sharp line characteristic of fast relaxation is obtained.

The broadening of the p.m.r. lines by the ^{14}N nucleus is attributed⁵¹ to incomplete removal of the ^{14}N - H coupling, rather than a shortening of the proton relaxation time by the ^{14}N relaxation.

It is clear from figures 2.1 and 2.2 that the effects of the ^{14}N quadrupole and of proton exchange upon the p.m.r. spectrum are broadly similar. Thus a broad p.m.r. peak may be characteristic of either effect. ^{14}N double resonance may be used to distinguish between the two since only quadrupole broadening is sharpened by it. The effect of changing the temperature may also be used, since the rate of exchange is increased and the rate of ^{14}N relaxation is reduced with increased temperature. In the former case the peak should be sharpened, in the latter it should be broadened.

2.5 The p.m.r. spectra of pyridine and pyridinium

Both pyridine and pyridinium have been the subjects of a number of p.m.r. experiments^{52,53}. The proton chemical shifts of the complex $(\text{py}_2\text{H})^+$ are not expected to be very different from those of the individual species, except in the N-H proton resonance, since H-bond formation has only a marginal effect upon the p.m.r. shifts of the C-H protons. In addition, intermolecular exchange between the complex and its constituents is rapid and averaging over the three species will occur.

There is a significant effect⁵⁴ in the coupling of the ^{14}N nucleus with the C-H protons upon H-bonding

since the ^{14}N quadrupole relaxation is increased leading to broadening of the C-H proton resonances.

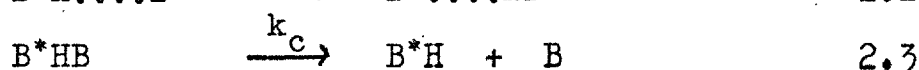
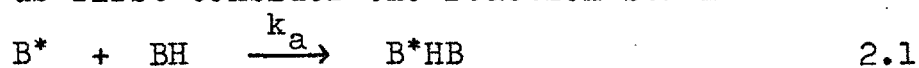
A pronounced solvent effect⁵⁵ upon the chemical shift of the ring protons in pyridine has been ascribed to self association in pure base. This is likely to make experiments using pyridine as solvent unsatisfactory and none are reported in this work.

In the present context, the most significant proton resonance signal is that of the N-H proton. It is likely to be strongly affected by H-bond formation. In solutions of free pyridinium ions in which proton exchange has been suppressed by the presence of a strongly acidic solvent (e.g. trifluoroacetic or formic acid), a triplet is observed^{45,53} with a ^{14}N -H coupling constant of about 70 Hz. The fact that a triplet can be observed is at least indicative that the ^{14}N environment is sufficiently symmetric for slow relaxation of the ^{14}N quadrupole. Any broadening observed is therefore likely to be due to exchange.

2.6 The measurement of exchange rates in symmetric complexes by p.m.r.

The effects of exchange and of the ^{14}N nucleus upon the p.m.r. spectrum of the N-H proton suggest a means of measuring the exchange rate between two bases of the N-H proton.

Let us first consider the reaction scheme:

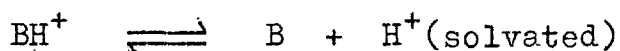


In this scheme charges are omitted for simplicity and the asterisks are used to distinguish between the two identical base molecules. It can be seen that the scheme divides into two different proton transfer reactions. The first, represented by 2.2, is the intramolecular transfer of the proton between the two wells of the double minimum potential. It is known that the complex, BHB, has a finite lifetime during which it is quite likely that reaction 2.2 will occur a number of times.

The second proton transfer reaction is that represented by reactions 2.1 and 2.3, and may be termed intermolecular. The postulation of a double minimum potential is not necessary for this reaction, although if one exists, reaction 2.2 is necessary to transfer the proton from one base to the other before dissociation occurs. However, as indicated above, reaction 2.2 will not be rate determining.

The effect of these exchanges upon the p.m.r. spectrum of the N-H proton is as follows. It is known that the coupling constant in the pyridinium ion between the ^{14}N and proton spins is about 70 Hz⁴⁴. If the rate of proton exchange is faster than this, and it seems likely to be so for both mechanisms, then no ^{14}N -H coupling, either splitting or broadening, will be observed. The difference in the chemical shift of the N-H proton resonance between the free donor and the H-bonded complex is in the region of 5 p.p.m. (300 Hz on a 60 MHz instrument) and again, the intermolecular transfer rate is faster than this, under normal conditions.

Chemical reaction rates may however be slowed down by decreasing the concentrations of the reactants. If we suppose that reaction 2.1 occurs at a rate of the order of the rate of collisions, then $k_a \sim 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. The lower concentration limit for the detection of the N-H proton is $\sim 10^{-3} \text{ mol l}^{-1}$, and we wish to slow the reaction rate to about 10^2 s^{-1} . Then the value of $[B]_0$ must be $\sim 10^{-5} \text{ mol l}^{-1}$ and an equilibrium constant for the formation of the complex of $\sim 3 \text{ l mol}^{-1}$, gives $[BHB] \sim 3 \times 10^{-8} \text{ mol l}^{-1}$. At these concentrations the complicated effects of the dissociation of the donor cation:



make accurate estimation of the concentrations most difficult and experiments of this kind do not appear at present to be feasible. It is in any case not possible to slow the rate of intramolecular exchange by this means.

It is of interest at this point to note that the figures given in the previous paragraph imply a value of $k_c = 3 \times 10^9 \text{ s}^{-1}$ and hence a lifetime of the complex cation of $3 \times 10^{-10} \text{ s}$. Calculations of the rate of k_b indicate a value of about 10^{12} s^{-1} . Thus reaction 2.2 occurs about 300 times in the lifetime of the complex.

Joop and Zimmermann⁵⁶ observed that the N-H proton resonance of imidazole was broadened by dilution in acetone, and sharpened by the addition of the potassium salt of the imidazole anion. They interpreted these facts in terms of an exchange sharpening of the intramolecular type, and cited them as evidence of a double minimum potential. The facts may equally well be interpreted as the result of intermolecular proton transfer which, as has

been shown, does not necessitate the existence of a double minimum potential.

2.7 Introduction to the experiment

Although no data on intramolecular exchange rates can be obtained it was considered useful to derive some data on the equilibrium constants and chemical shifts of the symmetric complexes, as a guide to the strength of such complexes.

Measurement of chemical shift data was carried out in dilute solutions in acetonitrile for the reason outlined in section 2.5. Unlike those spectroscopic techniques in which all species in solution contribute to the spectrum, the resonance of the N-H proton is the resultant of only two of the three equilibrium species. Therefore it is unnecessary to use high concentrations of donor and acceptor in order to get a reasonable concentration of complex. Instead, the resonance position is a measure of the proportion of added donor in solution which is complexed; a proportion which increases as more acceptor molecules are added. The concentration of added donor can be as small as is compatible with detection and accuracy of measurement.

In the limit of fast exchange, as has already been mentioned, the position of a resonance peak due to the exchanging proton is at a weighted average between the two environments:

$$\delta = \frac{\delta_{BH}[BH] + \delta_{BHB}[BHB]}{[BH]_0}, \quad 2.4$$

$$\text{and since } [BH]_0 = [BH] + [BHB], \quad 2.5$$

$$\delta = \delta_{BH} + (\delta_{BHB} - \delta_{BH}) \frac{[BHB]}{[BH]_0} \quad 2.6$$

The effects of exchange and of the ^{14}N quadrupole relaxation normally make detection of the N-H proton resonance impossible in solutions containing free salt alone. Thus δ_{BH} is an unknown quantity. A trace of acceptor in the solution increases exchange to the fast limit, consequently sharpening the peak.

In each run, to a solution containing a constant concentration of added donor ($[BH]_0$), a series of additions of base were made. Thus the complex concentration was increased since

$$K_c = \frac{[BHB]}{[B][BH]} \quad 2.7$$

It is common⁵⁷ to assume $[B] \gg [BHB]$, however an analysis⁵⁸ of the inherent error in this assumption for values of $K > 1\text{M}^{-1}$ shows that the assumption is often made rashly. The advent of computer curve-fitting techniques, such as that used here, should render the assumption unnecessary since this assumption has the sole advantage of enabling results to be obtained from a linear plot. Thus the treatment in this work involves no approximations.

It can be simply shown that equation 2.7 exactly leads to

$$[BHB] = \frac{Q - \sqrt{Q^2 - 4[B]_0[BH]_0}}{2} \quad 2.8$$

$$\text{where } Q = [B]_0 + [BH]_0 + K_c^{-1} \quad 2.9$$

Substituting 2.8 into 2.6 gives the chemical shift in terms of the three constants (K_c , δ_{BH} and δ_{BHB}) and the two variables ($[BH]_0$ and $[B]_0$). In each run, however, $[BH]_0$ was constant and hence δ was a function of $[B]_0$ alone.

Results were analysed by means of a computer program, DARWIN, which is given in appendix 1. DARWIN obtains the values of the three parameters, K_c , δ_{BH} and δ_{BHB} , for each experimental run by finding the best curve, δ vs $[B]_0$ which fits the experimental points.

2.8 The Experimental Results

2.8.1 Observations of p.m.r. spectra

Solutions of free donor to which no acceptor has been added give rise to an N-H proton resonance peak broadened by exchange at an intermediate rate. Addition of excess acid to these solutions slows exchange and allows the observation of the N-H proton triplet, split by coupling with the ^{14}N nucleus. Addition of proton acceptor to the free donor solution sharpens the N-H proton resonance peak and it moves downfield. It is to be expected that, even in free donor solutions, sufficient dissociation occurs under all conditions unless such dissociation is suppressed by the addition of excess acid. In all runs in which base was added in successive portions to donor solutions, the N-H proton resonance peak was observed to move downfield. No further sharpening of this peak was observed after the addition of the first portion of base.

2.8.2. Results of the calculations using DARWIN

The overall results for six systems are given in table 2.1. In general it was found that the program DARWIN was able to obtain values of the three parameters to a high degree of accuracy for the individual runs. Errors in K_c , δ_{BHB} and δ_{BH} were of the order of 0.1 l mol^{-1} , 0.04 and 0.02 p.p.m. respectively. The calculated curve fitted the experimental points very closely with an r.m.s. deviation in δ of approximately 0.02 p.p.m. It was noticed early in the experiments that there was a good correlation between K_c and δ_{BHB} in runs which had not been taken to a sufficiently high value of $[B]_0$. In these cases the program was unable to find a line of best fit and subsequent runs were extended to higher values of $[B]_0$.

The overall results presented do not show such a high degree of accuracy since there were discrepancies in the range of results for each system. Only in the 3-Cl pyridine system are the discrepancies larger than 10%. Several explanations, for the wide range of results within each system, were suggested; but none was satisfactory. It was proposed that the dissociation of proton donor to give free base and solvated protons might be a more serious problem. If this were the case the value of $[BH]_0$ used in the calculation would be too high and that of $[B]_0$ too low. The effect should vary in a consistent way with $[BH]_0$ but it does not do so and was discounted. A more serious effect would be the presence of water in the sample. This was studied in some detail and the results are presented in section 2.9. Observed

TABLE 2.1 EQUILIBRIUM CONSTANT AND CHEMICAL SHIFT DATA FOR SYMMETRIC COMPLEXES

<u>Base</u>	<u>Counter-ion</u>	⁵⁹ <u>pK_a</u>	<u>K_c</u> (<u>l mol⁻¹</u>)	<u>δ_{BH}</u> (<u>p.p.m.</u>)	<u>δ_{BHB}</u> (<u>p.p.m.</u>)	<u>Δδ</u> (<u>p.p.m.</u>)
3,5-dimepy	BF ₄ ⁻	6.14	5.6 ± 0.3	12.2 ± 0.4	17.3 ± 0.3	5.1 ± 0.3
4-mepy	ClO ₄ ⁻	6.02	3.4 ± 0.2	12.5 ± 0.2	18.3 ± 0.2	5.8 ± 0.2
py	BF ₄ ⁻	5.17	3.4 ± 0.1	12.7 ± 0.1	18.1 ± 0.1	5.4 ± 0.1
py	ClO ₄ ⁻	5.17	3.0 ± 0.2	12.8 ± 0.1	18.2 ± 0.2	5.4 ± 0.2
qu	ClO ₄ ⁻	4.90	2.6 ± 0.2	13.7 ± 0.1	17.0 ± 0.1	3.3 ± 0.1
3-Clpy	ClO ₄ ⁻	2.84	1.5 ± 0.2	12.6 ± 0.1	16.6 ± 0.2	4.0 ± 0.2

inconsistencies in the results did not agree with any of the results of the added-water tests. It seems that there is no satisfactory explanation of the wide-ranging results.

2.9 The effect of water upon the N-H proton resonance

2.9.1 Experimental results

Qualitative experiments were carried out in which solutions, prepared in the normal way, were doped with water. In solutions containing added donor and acceptor (i.e. $[B]_0 \neq 0$) the effect of a very small amount of water was to shift the N-H proton resonance upfield. Addition of more water, effectively saturating the exchanging proton, made the characteristically low-field peak of the N-H proton disappear. Instead the peak due to water at about 4.2 p.p.m. was observed.

For solutions where $[B]_0 = 0$ addition of a minimal amount of water sharpened the N-H proton peak and shifted it upfield. Added base served to shift this peak downfield.

These observations are consistent with the suggestion that water acts as another species in the averaging process that takes place between free donor and the complex. Two effects make the presence of water a particular problem. Firstly the chemical shift of water, δ_w , is very low so that a small amount has a marked effect on the position of the averaged signal. Secondly the low molecular weight of water means that the concentration of protons is high; a small amount of water can move the N-H proton peak a great deal.

2.9.2. Calculations

A simulation of the effects of water upon the results obtained from the DARWIN program was carried out. Two points of interest were considered. Most simply, what is the largest amount of water that can be present before the parameters obtained by curve fitting are incorrect? Secondly, since experiments were carried out with three or four runs simultaneously at different values of $[BH]_0$, using chemicals from the same batches, could the effect of water be detected by differences in the results of these runs?

A single set of parameters was selected and the results of a series of runs at different values of $[BH]_0$ were calculated, giving simulated raw data for chemical shifts against $[B]_0$. The chemical shift of water was assumed to be 4.0 p.p.m. Three separate simulations, with water in each of the three components of the solutions individually, were performed. The fresh data, averaged with varying concentrations of water, was treated by DARWIN in the usual way and values for the three parameters were obtained. Results are shown in table 2.2. The concentrations of water shown are in mol. per cent in the component named.

It is immediately clear that below a certain limit (10^{-4} , 10^{-3} and 10^{-1} mol % in solvent, base and salt respectively) the effect of water is negligible. The presence of water in salt is not detectable by the present method since the proportion of water to salt does not change. This is of particular concern since the salt is the most hygroscopic component and the only one that has

TABLE 2.2. EQUILIBRIUM CONSTANT AND CHEMICAL SHIFT DATA
CALCULATED TO SHOW THE EFFECT OF CONTAMINATION BY WATER OF
INDIVIDUAL COMPONENTS OF THE SOLUTION.

$[H_2O]$ (mol %)	$[BH]_o$ (mol ℓ^{-1})	K_c (ℓ mol $^{-1}$)	δ_{BH} (ppm)	δ_{BHB} (ppm)	$\Delta\delta$ (ppm)
No water					
-	-	3.30	12.78	18.14	5.36
Water in solvent					
0.01	0.10	3.28	12.46	17.62	5.16
0.01	0.02	3.30	11.37	15.87	4.50
0.001	0.10	3.32	12.74	18.08	5.34
0.001	0.02	3.29	12.62	17.88	5.26
0.0001	0.10	3.30	12.78	18.13	5.35
0.0001	0.02	3.30	12.76	18.11	5.35
Water in base					
0.01	0.10	3.34	12.78	18.09	5.31
0.01	0.02	3.56	12.78	17.88	5.10
0.001	0.10	3.31	12.78	18.13	5.35
0.001	0.02	3.31	12.78	18.12	5.34
Water in salt					
1.0	0.10	3.29	12.61	17.87	5.26
1.0	0.02	3.28	12.61	17.87	5.26
0.1	0.10	3.32	12.76	18.10	5.34
0.1	0.02	3.30	12.76	18.11	5.35

to be exposed to the atmosphere in weighing. Since in the solution, in which $[B]_0 = 0$, the presence of water can only be due to salt and solvent, we should expect to be able to detect these by the sharpening of the N-H proton resonance peak as discussed in section 2.9.1. In no experiment was such sharpening observed. Since the presence of water in base implies an increasing water concentration as the run proceeds, the addition of sufficient damp base may cause the curve of δ_{obs} vs $[B]_0$ to reach a maximum and then decrease. It is possible that the evidence of water could be indicated by the deviations of the experimental points from the best calculated curve. Deviations in these model calculations were all less than the experimental errors observed.

Of the effects of water shown in table 2.2, none was observed in the course of the experiments. It seems therefore that water was not the cause of the discrepancies between runs unless the systematic procedures adopted failed to reveal its presence.

2.10 Discussion

The observations described in section 2.8.1 are clearly explicable in terms of the intermolecular exchange discussed in section 2.6. The spin-spin coupling between ^{14}N and ^1H is only observed if the lifetime of the free proton donor is sufficiently long. The concentration of proton acceptor is decreased by adding acid; the rate of association, $k_a[B][BH]$, is then decreased with a consequent increase in the lifetime of BH. As free base is added to the solution, the rate of association

is increased, and the lifetime of free BH is decreased, sharpening the N-H proton resonance by exchange.

Conclusions derived from the data presented in table 2.1 must be accompanied by a warning that such conclusions, based on so few data, must necessarily be tentative. The most outstanding conclusion is that the equilibrium constant for complex formation increases with increasing base strength. Trends in the chemical shifts of the N-H protons show a downfield movement for the free donor (excluding 3-Clpy) and an upfield change for the hydrogen-bonded complex (excluding 3,5 dimepy) with decreasing base strength.

A rationalisation of these results is illustrated in figure 2.3. The reason that one heterocyclic nitrogen base is stronger than another is partly that the lone pair electron cloud upon the nitrogen is larger. This is due to the presence of electron pushing or withdrawing groups on the ring. The electron cloud of the stronger base is thus more able to shield the proton in the acid and the resonance for that proton occurs at higher field.

The approach of a base to its conjugate acid leads to a polarisation of the B-H bond and the proton is drawn into a region of lower electron density. If the double minimum potential is postulated, the proton density at the centre of the bond is small. The stronger the base, the greater is the polarisation and the downfield shift of the bridging proton resonance. This explanation fails to take into account the strength of the donor base molecule which would be expected to resist the polarisation more

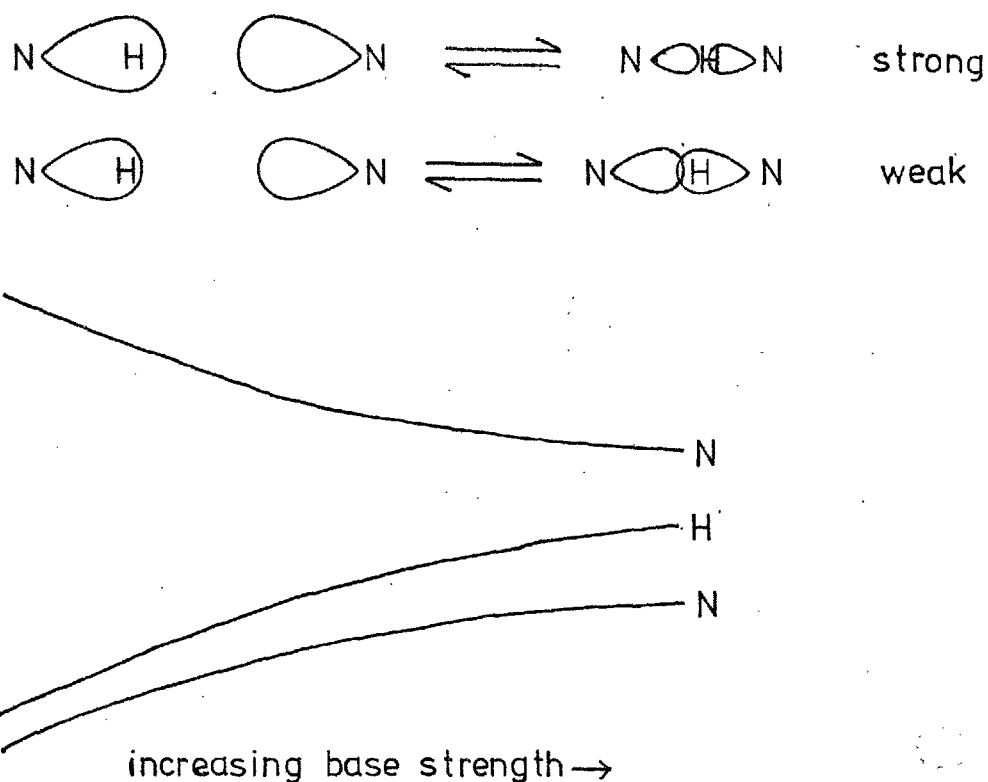


Figure 2.3. The effect of increasing base strength upon the N-N and N-H distances and hence complex strength.

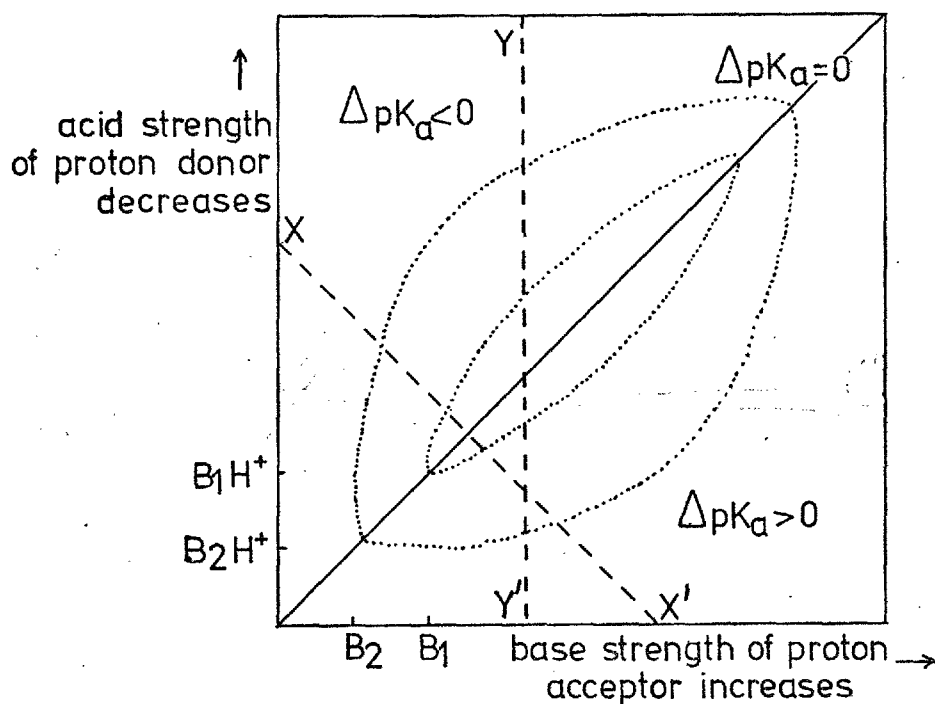


Figure 2.4. Contour diagram of complex strength with respect to the uncomplexed donor and acceptor against acid and base strength of the two constituents.

strongly. The results indicate that the attractive nature of the acceptor base is more important than that of the donor base.

The conclusion that stronger bases form stronger symmetric complexes, $(\text{BHB})^+$, is in agreement with other results^{20,23} for nitrogen bases in acetonitrile. Whilst it is comparatively simple to show that the complex $(\text{B}_1\text{H}\dots\text{B}_1)^+$ is more stable than $(\text{B}_1\text{H}\dots\text{B}_2)^+$ compared to the free donor and acceptor, the relative strengths of symmetric complexes are less easily predicted.

Figure 2.4 shows a suggested energy surface for the generalised complex $\text{B}_1\text{H}\dots\text{B}_2$ where B_1 is a stronger base than B_2 . Note that both $\text{B}_1\text{H}^+ + \text{B}_2$ and $\text{B}_1 + \text{B}_2\text{H}^+$ give the same complex $(\text{B}_1\text{H}\dots\text{B}_2)^+$. Figures 2.5 and 2.6 are cross sections across XX' and YY' respectively. It is important that the basis from which all energies are measured is agreed since it is clear that the symmetric complex $(\text{B}_1\text{H}\dots\text{B}_1)^+$ is the most stable with respect to $\text{B}_1\text{H}^+ + \text{B}_1$, yet the least stable with respect to $2\text{B}_1 + \text{H}^+$.

The asymmetry of the complex is defined by

$$\Delta\text{pK}_a = \text{pK}_a (\text{acceptor}) - \text{pK}_a (\text{donor}). \quad 2.10$$

For symmetric complexes ($\text{B}_1 = \text{B}_2$): $\Delta\text{pK}_a = 0$, but for asymmetric systems ΔpK_a may be either negative - in which case the donor moiety, B_1 , is a stronger base than the acceptor, B_2 , or positive - when the base strengths are reversed. In the latter situation proton transfer should occur if a double minimum potential exists. Thus the potential surface is symmetrical about the line $\Delta\text{pK}_a = 0$.

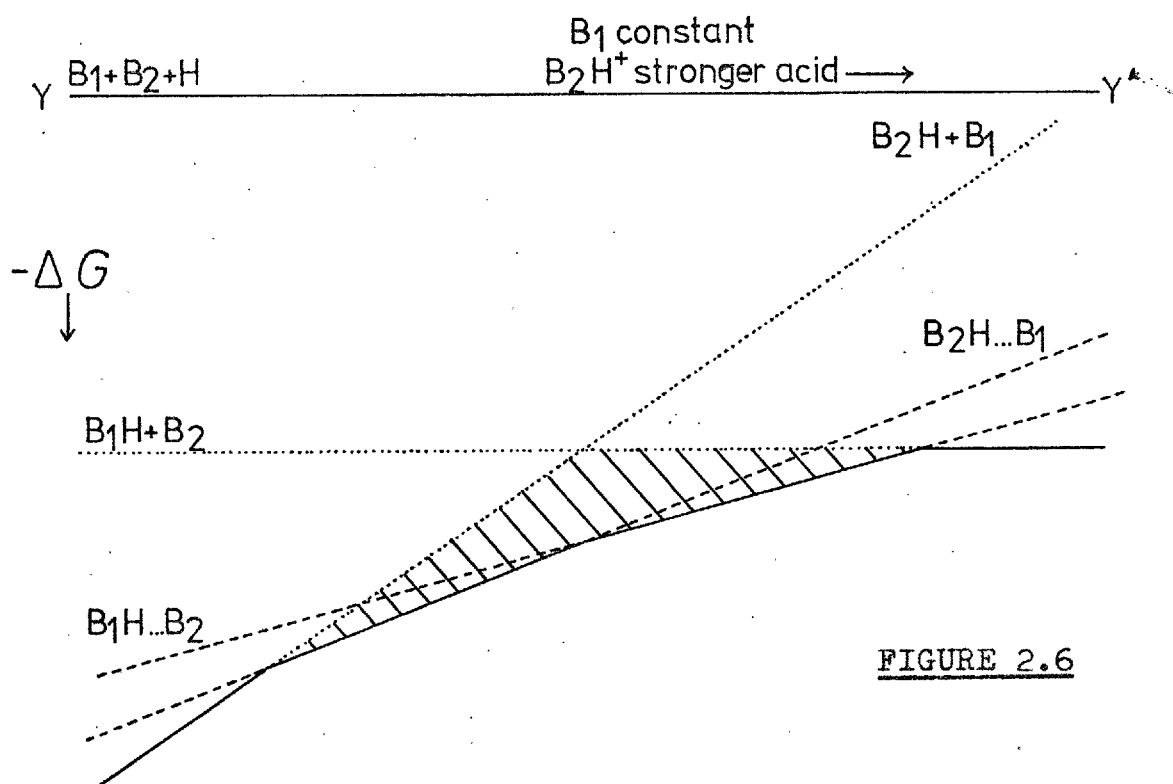
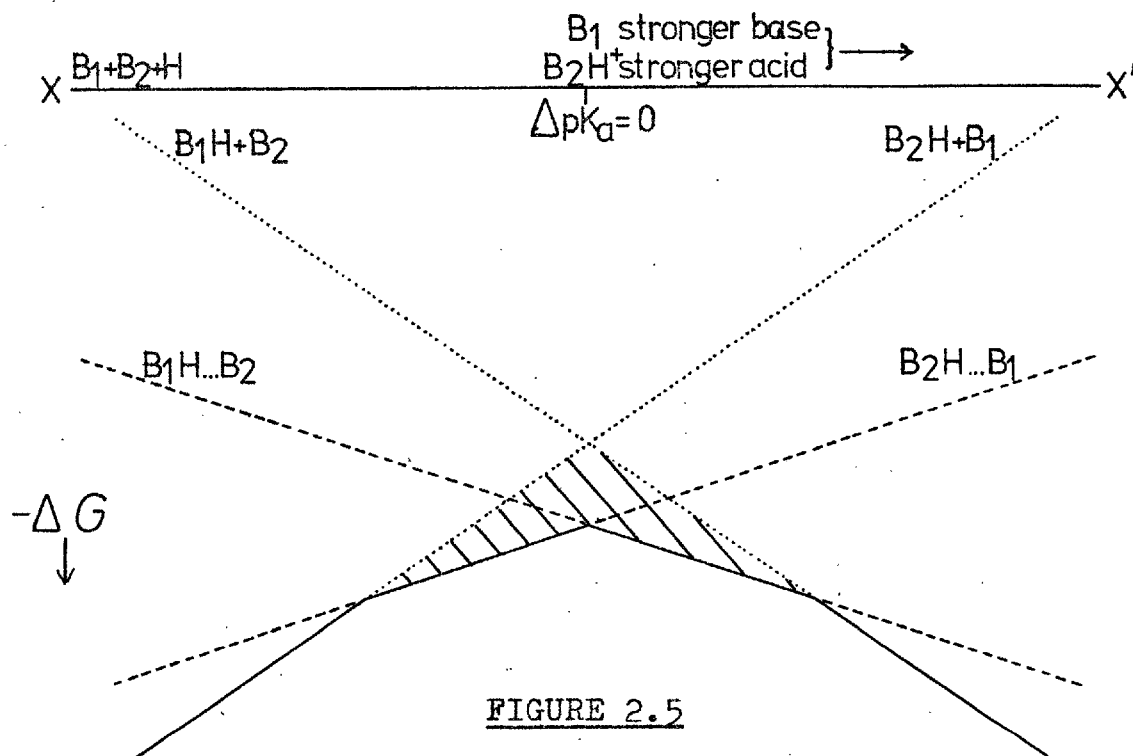


Figure 2.5. Section along xx' of figure 2.4, with respect to the two free base molecules and the proton. The shaded area is that plotted in figure 2.4.

Figure 2.6. Section along yy' of figure 2.4, as in figure 2.5.

Figure 2.5 shows the effect of continuously increasing the base strength of B_1 and decreasing the base strength of B_2 . The energy zero is shown for the separated species $B_1 + B_2 + H^+$. The energy curves for the reactions

$$B_1 + B_2 + H \rightleftharpoons B_1H + B_2 \quad 2.11$$

and

$$B_1 + B_2 + H \rightleftharpoons B_1 + B_2H \quad 2.12$$

are shown to fall as the base strengths of B_1 and B_2 , respectively, are increased. The strength of the hydrogen-bonded complex depends upon which side the proton is located. The complex $(B_1H \cdots B_2)^+$ is strongest, with respect to the energy zero, when B_1 is a strong base and B_2 a strong acid. At the point where $B_1 = B_2$ both the acid-base curves cross as do the complex formation curves. This is the point in which most interest lies at present. The hydrogen bond strength with respect to the dissociated donor and acceptor is indicated by the shaded area. The diagram also shows that if the base strengths of B_1 and B_2 are too unequal, the hydrogen-bonded complex is unstable.

Figure 2.6 illustrates the case where the strength of one moiety is constant. The principal difference between figures 2.5 and 2.6 is that the curve for $B_1 \cdots HB_2$ falls with increasing base strength of B_1 .

It was hoped that such arguments might shed some light upon the nature of the relationship between complex and base strengths. However the lack of information upon the actual shapes of the curve in figures 2.6 and 2.7 prevents such deductions. The argument is a general one but it can only apply to individual systems and comparisons between, for example, phenol-phenate and pyridine-pyridinium complexes are misleading⁶⁰.

CHAPTER 3

3. ELECTRONIC ABSORPTION AND FLUORESCENCE STUDIES OF THE QUINOLINE SYSTEM

3.1 Introduction

The role of fluorescence spectrophotometry in hydrogen bonding was briefly discussed in section 1.6.3. Such work has previously involved the study of the quenching of fluorescence in asymmetric systems with no net charge. It is suggested that such investigations might reasonably be extended to the symmetric systems of the present study, with a view to obtaining a rate constant for the prototropic reaction in the excited state. An expanded version of figure 1.7 is given in figure 3.1. This shows that if it were possible to excite the proton donor or acceptor species preferentially then fluorescence characteristic of the four excited species might be observed, following equilibration in the excited state.

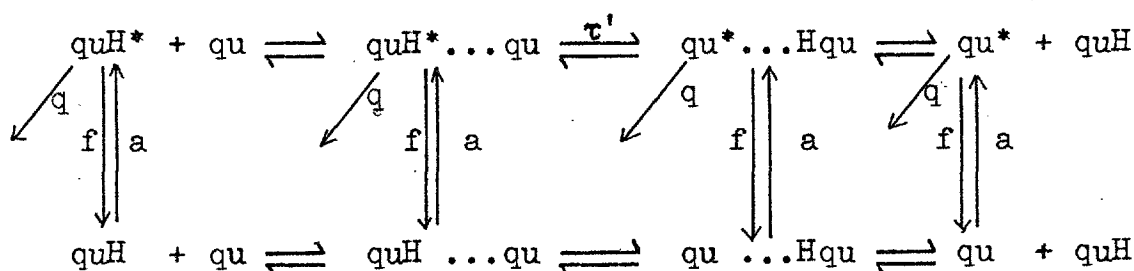


Figure 3.1 A suggested fluorescence scheme for the quinoline system. The equilibrium, τ' , may occur by either proton or exciton transfer.

It seems unlikely that a system could be found in which either fluorescence or absorption of the hydrogen bonded complex could be distinguished from those of the free species. However if, for example, the solution were to be irradiated at the characteristic frequency of BH^+ and fluorescence characteristic of B were to be observed, then we should expect prototropism in the excited state to be involved, unless the excitation could cross the hydrogen bond. Whilst the scheme proposed may prove too complicated for static fluorescence experiments to unravel, we might hope that time-resolved spectrophotometry would reveal the presence of different species at different times after the excitation pulse.

The principal criterion for selection of a system for these studies is that the absorption and fluorescence spectra of the base and its conjugate acid should be as different as possible. As well as for the reasons given above, such a system would enable us to swamp the solution with the non-absorbing species and hence step-up the complex concentration.

Quinoline was chosen as the base in the present experiments. Figures 3.2 and 3.3 show that its conjugate acid has a considerably greater absorption in the 315 nm region and a lower absorption in the 270 nm region. This system is far from perfect, however, since both species have an appreciable absorption in the 250-350 nm region, preventing the use of a swamping method.

3.2 The absorbance spectrum of the complex cation

Normal measuring techniques, in dilute acetonitrile solutions, were used to measure the absorption spectra of quinoline and its conjugate acid (figures 3.1 and 3.2). The observed maxima are at the positions given by Mason⁶¹ (his quinoline was in cyclohexane); the extinction coefficients are however about 25% greater than his at 313 nm and approximately the same for the base at 270 nm. These are ($\pi^* \leftarrow \pi$) bands; the ($\pi^* \leftarrow n$) bands are much weaker and obscured at the long wavelength end of the main bands. The two bands in quinoline are due to transitions from the two highest occupied π -orbitals to the lowest unoccupied π -orbital. In the acid the energy of the highest occupied π -orbital falls to that of the second highest such orbital and there is an equal drop in the energy of the lowest unoccupied π -orbital, merging the two bands.

It is of particular interest in the present study to establish whether or not there is any difference between the u.v. spectrum of the complex cation, $(qu_2H)^+$, and the sum of the spectra of its two constituents. The low equilibrium constant of complex formation reported in chapter 2 would hinder any conventional measurement of the u.v. spectrum of the complex in dilute solution, so a novel approach, using relatively concentrated solutions, was developed. This method necessitated the use of extremely short path-length cells, whose absolute path-length was unknown.

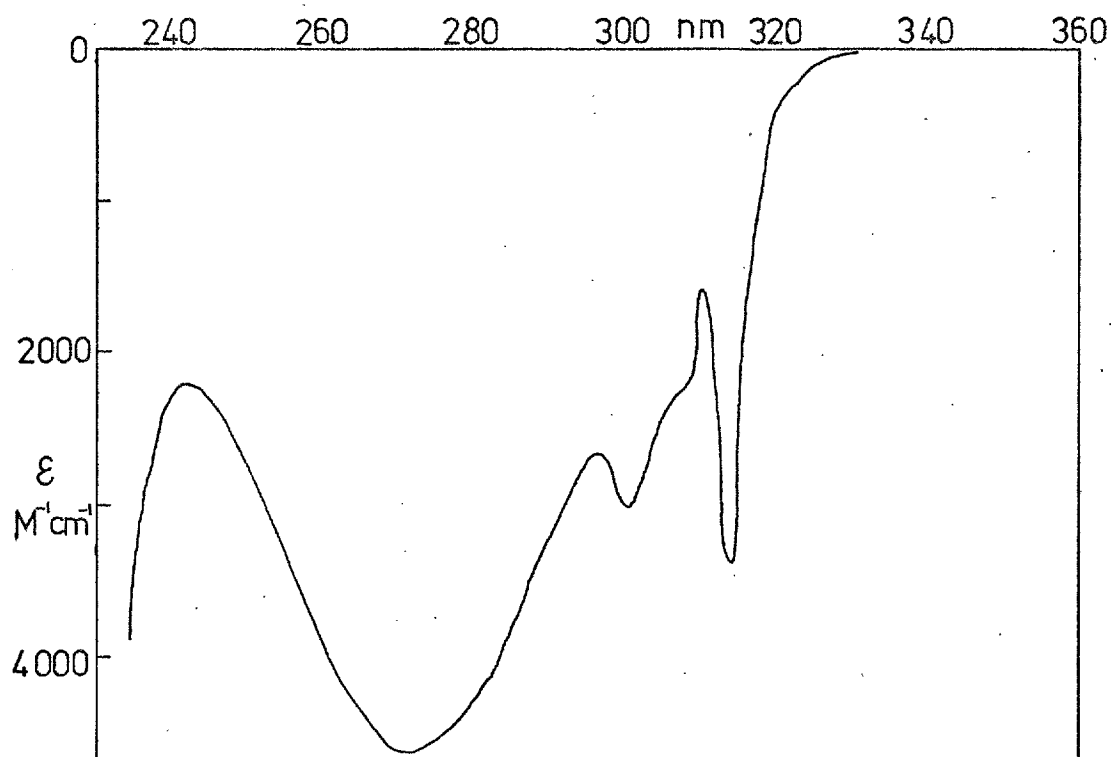


Figure 3.2. The ultra-violet spectrum of quinoline.

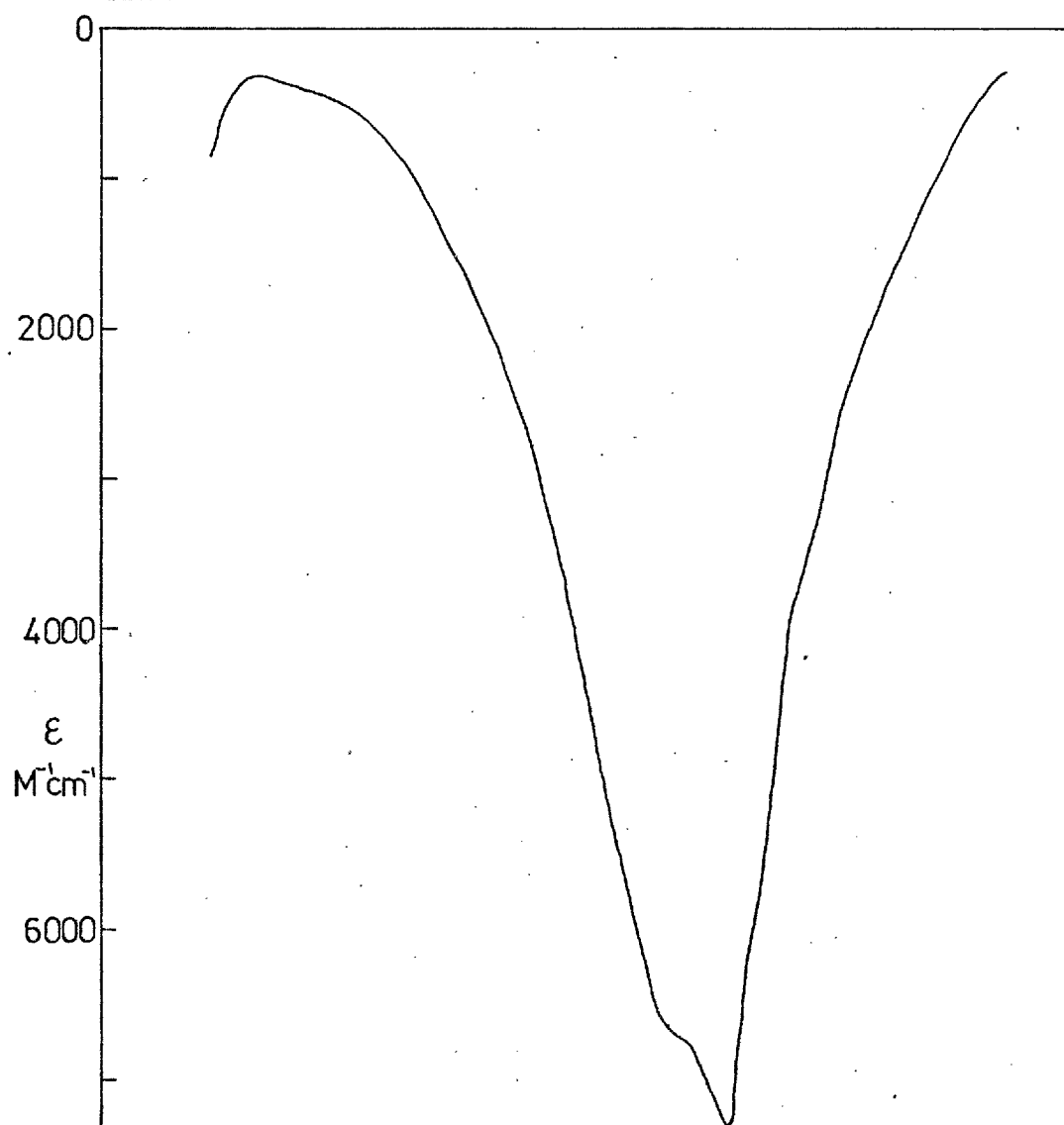


Figure 3.3. The ultra-violet spectrum of the quinolinium ion.

3.2.1 Calculation of the u.v. absorption spectrum of the complex

For a solution, with pathlength l cm, containing $[B]$, $[BH]$ and $[BHB]$ mol l^{-1} base, acid and complex respectively, the absorbance, A_λ , at a wavelength, λ nm, is given by

$$A_\lambda = (\epsilon_{\lambda B}[B] + \epsilon_{\lambda BH}[BH] + \epsilon_{\lambda BHB}[BHB])l \quad 3.1$$

where the ϵ_λ 's are the relevant extinction coefficients, at λ nm, in l mol $^{-1}$ cm $^{-1}$.

For a second solution with different concentrations and a different pathlength, the absorbance is

$$A'_\lambda = (\epsilon_{\lambda B}[B]' + \epsilon_{\lambda BH}[BH]' + \epsilon_{\lambda BHB}[BHB]')l' \quad 3.2$$

Combining equations 3.1 and 3.2 we obtain

$$\begin{aligned} \epsilon_{\lambda BHB} &= \left\{ \frac{A_\lambda}{l} - (\epsilon_{\lambda B}[B] + \epsilon_{\lambda BH}[BH]) \right\} \frac{1}{[BHB]} \\ &= \left\{ \frac{A'_\lambda}{l'} - (\epsilon_{\lambda B}[B]' + \epsilon_{\lambda BH}[BH]') \right\} \frac{1}{[BHB]'} \end{aligned} \quad 3.3$$

$$\text{If we define : } \alpha_\lambda = \frac{\epsilon_{\lambda B}[B] + \epsilon_{\lambda BH}[BH]}{[BHB]} \quad 3.4$$

then rearranging 3.3 gives

$$\frac{A'_\lambda}{l'[BHB]'} - \frac{A_\lambda}{l[BHB]} = \alpha_\lambda' - \alpha_\lambda \quad 3.5$$

and hence

$$\frac{A'_\lambda [BHB]}{A_\lambda [BHB]'} = (\alpha'_\lambda - \alpha_\lambda) \frac{[BHB]l'}{A_\lambda} + \frac{l'}{l} \quad 3.6$$

Thus a plot of $\frac{A'_\lambda [BHB]}{A_\lambda [BHB]'}$ vs $(\alpha'_\lambda - \alpha_\lambda) \frac{[BHB]}{A_\lambda}$, for

different values of λ , should give a straight line

with gradient = ℓ' , and intercept = ℓ'/ℓ . With this knowledge $\epsilon_{\lambda\text{BHB}}$ can be calculated for both solutions using equation 3.3. A comparison of the two resulting spectra provides a method of checking this calculation.

3.2.2 The u.v. absorption spectrum of the complex

Using the equilibrium constant for complex formation obtained in chapter 2, ($2.7 \ell\text{mol}^{-1}$), [BHB] was calculated for the two solutions. The concentrations used are given in table 3.1. Figure 3.4 shows the satisfactory straight-line plot of equation 3.6.

	Solution 1	Solution 2
[B] ($\text{mol } \ell^{-1}$)	0.15	0.75
[BH] ($\text{mol } \ell^{-1}$)	0.68	0.26
[BHB] ($\text{mol } \ell^{-1}$)	0.27	0.52
ℓ (μm)	1.50	1.49

TABLE 3.1. Data used in the calculation of the u.v. spectrum of the complex, $(\text{qu}_2\text{H})^+$.

Evaluation was carried out at thirty-two wavelengths between 265 and 320 nm. The resulting spectra for the complex are shown in figure 3.5, with the sum of the spectra of the two independent components for comparison.

The most important result from this experiment is that there is no appreciable change in the absorption in the 300-320 nm region. There is however a red shift in the peak due to the quinoline base transition to the lowest unoccupied π -state from 270 nm to 297 nm. This

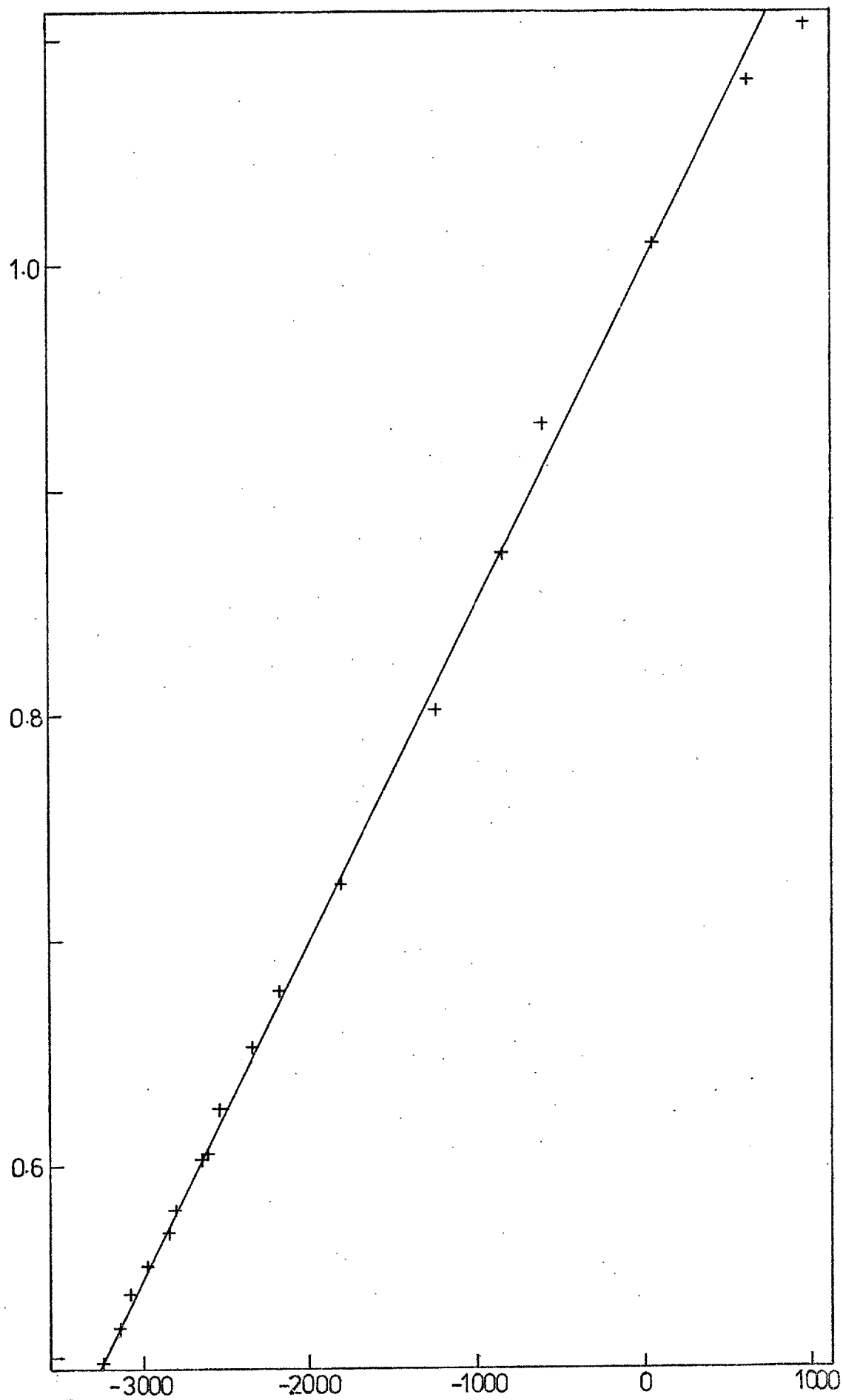


Figure 3.4. Plot of equation 3.6 for the quinoline system.

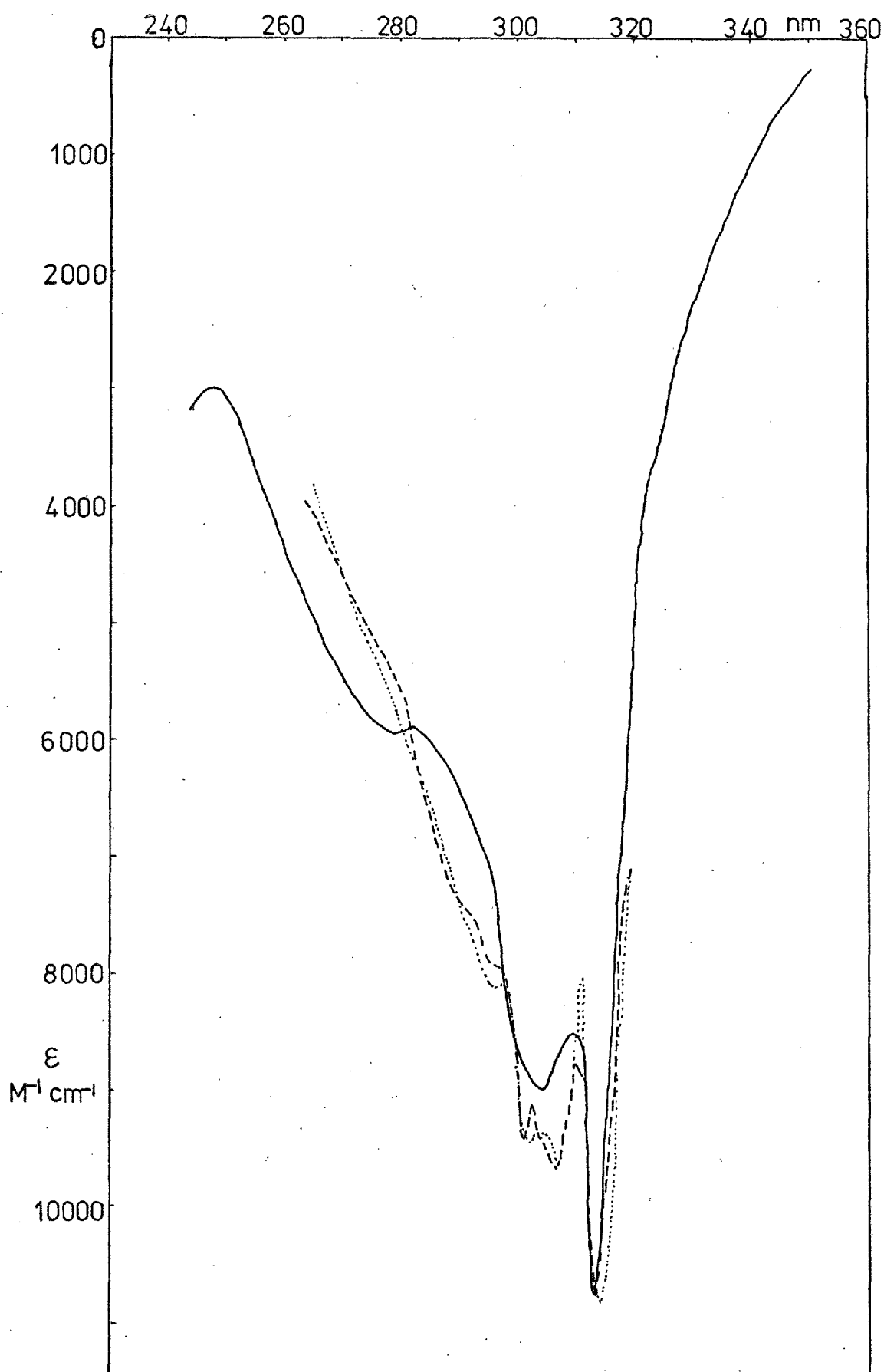


Figure 3.5. The ultraviolet spectrum of the symmetric quinoline complex obtained from the two solutions of table 3.1 (1:-- --, 2:.....). The solid line shows the sum of the spectra of the free base and salt for comparison.

strongly suggests that there is an overlap between the electron systems of the two quinoline ring systems, since the lowest unoccupied π -state is perturbed by complex formation. Any shift in the $\pi^* \leftarrow n$ transitions which are expected to undergo blue shifts, is obscured by the $\pi^* \leftarrow \pi$ massif.

3.3 Fluorescence experiments with the quinoline system

A number of fluorescence experiments⁶² with quinoline have shown that it does not exhibit fluorescence unless hydrogen bonded or protonated. This is because in the free base the ($n\pi^*$) state is lower than the ($\pi\pi^*$) state. Radiationless decay from the ($n\pi^*$) state is fast because of the proximity of the ($n\pi^*$) triplet state. Upon protonation the ($n\pi^*$) level moves above the ($\pi\pi^*$) state, from which fluorescence is observed. Of the species in the solutions studied in the present experiments, it is certain that fluorescence can only be due to quH^+ and $(qu_2H)^+$. It will be interesting to observe whether or not the complex cation gives two types of fluorescence due to the proton donor and acceptor.

Because of the unsatisfactory relationship between the absorption spectra of the base and cation, it was decided to carry out experiments with concentrated solutions. This required a novel cell arrangement so that the detector could observe the front face of the cell and in order to minimise inner filter effects⁶³.

3.3.1 Results of experiments

With excitation at 324 nm (at which the absorbance of the cation is more than ten times greater than that of the base), a fluorescence peak was observed at 413 nm. Figure 3.6 shows the variation in the reciprocal of the intensity of this peak with $[\text{quH}^+]$ in neat quinolinium fluorophosphate solutions in acetonitrile. The straight line gives the equation

$$\frac{1}{I_F} = (8. \pm 7.) \times 10^{-4} + (.244 \pm .004)[\text{quH}^+]_0 \quad 3.7$$

Points due to quD^+ are indicated in figure 3.4. They show no significant deviation from the straight line. Also shown is the effect of using acetonitrile containing 2% v/v water, which is not distinguishable.

Figure 3.7 indicates the observed variation in fluorescence intensity, under the same conditions, of a constant quinolinium concentration with added quinoline. Lines drawn by the least squares method for the three values of $[\text{quH}^+]_0$ are shown. For $[\text{quH}^+]_0 = 0.38\text{M}$ two lines are shown: one for all the experimental data and one for the first seven points ($[\text{qu}]_0 < 0.1\text{M}$). The values for gradients and intercepts are shown in table 3.2; errors due to the wide distribution of the experimental points are indicated.

The results for deuterated quinolinium solutions (quD^+) were not significantly different from those shown for the light salt.

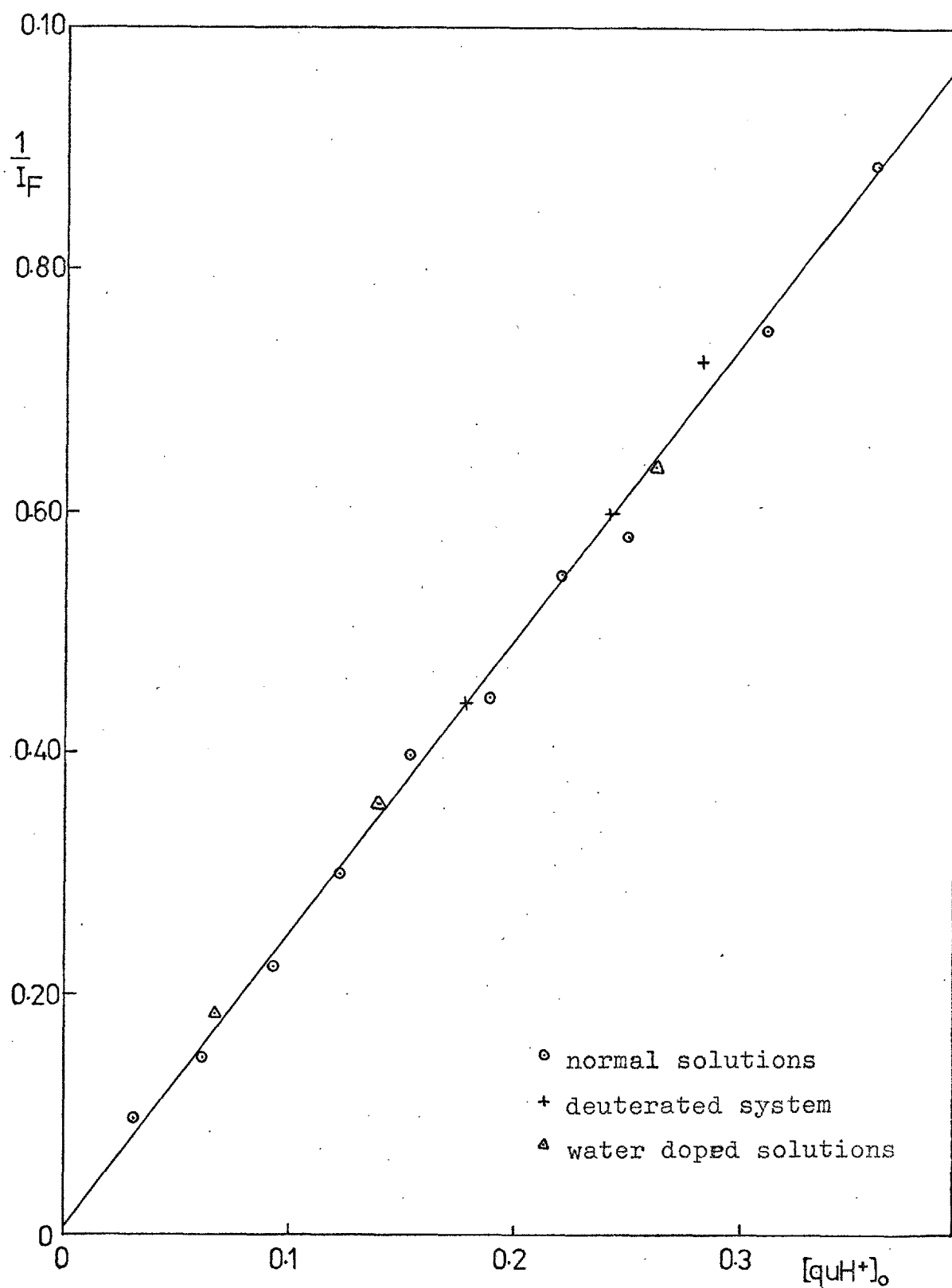


Figure 3.6. The effect of the concentration of a neat quinolinium solution upon the reciprocal of the fluorescence intensity.

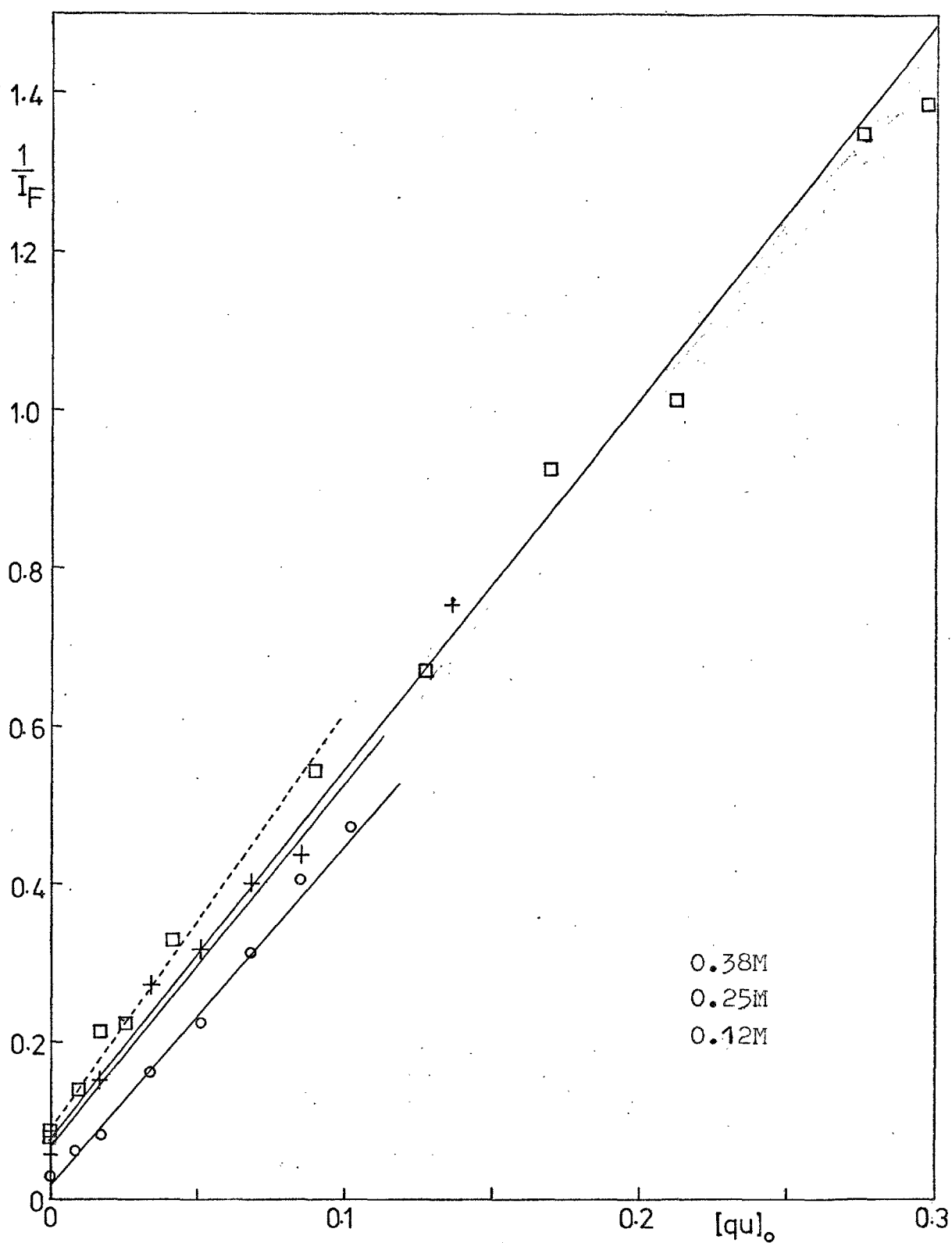


Figure 3.7. The effect of added base upon the reciprocal of the fluorescence intensity for constant quinolinium concentrations.

TABLE 3.2 Results from fluorescence experiments

$[\text{quH}^+]_0$ (mol ℓ^{-1})	$\partial\left(\frac{1}{I_F}\right) / \partial[\text{qu}]_0$ (ℓmol^{-1})	$\frac{1}{I_F} ([\text{qu}]_0 = 0)$ (arbitrary units)
0.12	4.3 ± 0.2	0.02 ± 0.01
0.25	4.6 ± 0.3	0.07 ± 0.02
(A) 0.38	4.7 ± 0.1	0.08 ± 0.02
(B) 0.38	5.3 ± 0.2	0.094 ± 0.001

(A) $\equiv$ result for all twelve points; (B) $\equiv$ result for $[\text{qu}]_0 < 0.1$.

The fluorescence peak observed at 413 nm has a constant width at half-height of $76(\pm 2)\text{nm}$. Because its shape is invariant with changing conditions it is assigned to the free quinolinium cation. It would be surprising if the fluorescence from the complex cation were identical (see figure 1.6). The scattered nature of the experimental results is due to the difficulty found in reproducing the conditions from one solution to the next, both in terms of the cell positioning and the excitation frequency.

3.3.2 Inner Filter Effects

It is important at the outset to establish that the observations reported in section 3.3.1 are not due to an experimental artefact. The experimental arrangement is shown in figure 3.8. The high concentrations used

may have the effect of (a) altering the size of the region of absorption and (b) absorbing the fluorescent light before it reaches the detector.

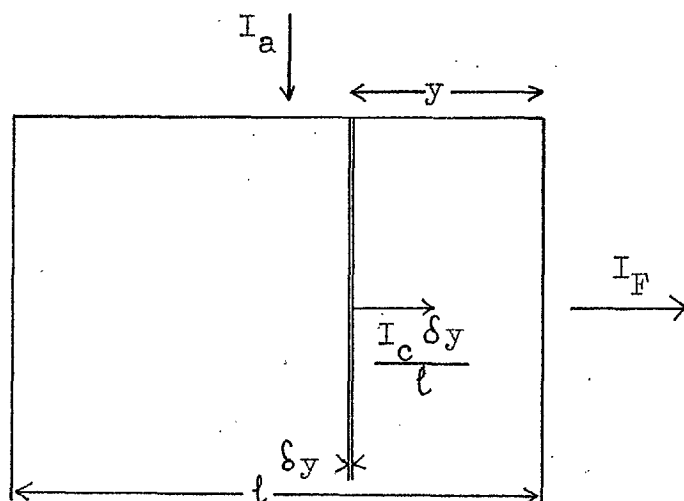


Figure 3.8 The experimental arrangement for fluorescence experiments. The abbreviations are defined in the text.

Let us first consider absorption. It is obvious that if a solution containing only one absorbing species absorbs very nearly all the incident light, then the number of excited molecules will be constant, and independent of the actual concentration. This is the situation in the case of the free quinolinium ion solutions since the amount of incident light which penetrates the 1 cm solution is negligible, because of the high concentrations used.

If a second absorbing solute (e.g. quinoline) is added, then the fraction of light absorbed by a constant concentration of quinolinium falls, as some of the incident light is absorbed by the quinoline. At the relevant

frequency the extinction coefficient of the complex is equal to the sum of the coefficients of its individual components; therefore complexing may be neglected in this argument. The total number of free quinolinium and complex cations excited is therefore proportional to

$$\frac{\epsilon_{\text{quH}^+[\text{quH}^+]}_0}{\epsilon_{\text{qu}[\text{qu}]}_0 + \epsilon_{\text{quH}^+[\text{quH}^+]}_0} \quad 3.8$$

where the ϵ 's are the extinction coefficients at the excitation frequency (324 nm).

The fluorescent light travels to the detector in a path perpendicular to the incident beam. The extinction coefficients of the species in solution at the fluorescent wavelength (413 nm) are unknown and small but it is likely that absorption will occur because of the high concentration. Suppose that fluorescence occurs from a small section of solution (figure 3.8), thickness δy and y cm from the exit face of the cell. If the exciting beam has a constant cross-section then the excitation process in that section is independent of the value of y . Let the total initial fluorescence intensity in the y -direction towards the detector be I_c . Then the fraction of this fluorescence, due to the section δy , that reaches the exit face of the cell is

$$\delta I_F = \frac{I_c \delta y}{l} \exp(-y \cdot \sum [x_i]_0 \epsilon'_i) \quad 3.9$$

where ϵ'_i is the extinction coefficient of the i th species at the fluorescence wavelength.

$$\text{hence } I_F = \frac{I_c}{\ell} \int_0^\ell \exp(-y \cdot \sum [x_i]_0 \epsilon_i') dy \quad 3.10$$

$$I_F = \left\{ \frac{1 - \exp(-\ell \sum [x_i]_0 \epsilon_i')}{\ell \cdot \sum [x_i]_0 \epsilon_i'} \right\} I_c \quad 3.11$$

For large values of $(\ell \cdot \sum [x_i]_0 \epsilon_i')$:

$$I_F = \frac{I_c}{\ell \sum [x_i]_0 \epsilon_i'} \quad 3.12$$

If we assume that there is no quenching of the excited quinolinium ions then the initial fluorescence intensity is proportional to the number of excited ions. Combining equations 3.8 and 3.12 gives:

$$I_F = \frac{B[quH^+]_0 \epsilon_{quH^+}}{\ell(\epsilon_{qu}[qu]_0 + \epsilon_{quH^+}[quH^+]_0)(\epsilon'_{qu}[qu]_0 + \epsilon'_{quH^+}[quH^+]_0)} \quad 3.13$$

where B is an overall constant of proportionality, which includes the fraction of irradiated molecules which are excited, the fluorescence efficiency, the geometric factor and the conversion factor from the true measured fluorescence intensity to I_F , which is in arbitrary units.

For solutions of free quinolinium ions ($[qu]_0=0$) equation 3.12 gives

$$\frac{1}{I_F} = \frac{\ell}{B} \cdot \epsilon'_{quH^+}[quH^+]_0 \quad 3.14$$

and hence using the experimentally obtained equation 3.7 and neglecting the small intercept value, with a cell width of 1 cm:

$$\frac{\epsilon'_{quH^+}}{B} = 0.244 \ell \text{ mol}^{-1} \text{ cm}^{-1} \quad 3.15$$

Expanding equation 3.13 gives

$$\frac{1}{I_F} = \frac{\ell}{\epsilon_{quH^+} B} \left\{ \epsilon_{qu} \epsilon'_{qu} \frac{[qu]_0^2}{[quH^+]_0} + (\epsilon_{qu} \epsilon'_{quH^+} + \epsilon_{quH^+} \epsilon'_{qu}) [qu]_0 + \epsilon_{quH^+} \epsilon'_{quH^+} [quH^+]_0 \right\} \quad 3.16$$

Figures for $\partial(1/I_F)/\partial[qu]_0$ given in table 3.2 indicate the possibility that lines for different values of $[quH^+]_0$ in figure 3.7 are parallel within the limits derived by the least squares method. For $[qu]_0 \ll [quH^+]_0$ equation 3.16 reduces to give

$$\frac{\partial(1/I_F)}{\partial[qu]_0} = \frac{\ell}{\epsilon_{quH^+} B} (\epsilon_{qu} \epsilon'_{quH^+} + \epsilon_{quH^+} \epsilon'_{qu}) \quad 3.17$$

from which we obtain, using $\partial(1/I_F)/\partial[qu]_0 = 4.5 \ell \text{mol}^{-1}$, $\epsilon_{qu} = 304 \ell \text{mol}^{-1} \text{cm}^{-1}$ and $\epsilon_{quH^+} = 3460 \ell \text{mol}^{-1} \text{cm}^{-1}$:

$$\frac{\epsilon'_{qu}}{B} = 4.48 \ell \text{mol}^{-1} \text{cm}^{-1} \quad 3.18$$

This derivation assumes that the observed variation of fluorescence intensity with concentration is entirely due to inner filter effects. There are two important points which indicate that this is not so:-

- (i) The inner filter effect explanation requires that $\epsilon'_{qu} = 18.4 \epsilon'_{quH^+}$ (equations 3.15 and 3.18);
- (ii) the shape of the observed fluorescence peak does not vary.

The spectral region of the fluorescence band is in the red end of the absorption bands of quinoline and quinolinium. Consequently the absorbance of the two

species cannot be measured as it varies rapidly in this region. It seems extremely unlikely however that the extinction coefficient of the free base could be more than that of the protonated base. Condition (i) therefore indicates that other factors must be included.

Point (ii) could only apply in this model if the ratio $\epsilon'_{\text{qu}}/\epsilon'_{\text{quH}^+}$ were constant across the whole region of the fluorescence peak. This is also an unlikely situation, suggesting that the fluorescence intensity variation cannot be entirely due to inner filter effects.

The fall in fluorescent intensity with increasing concentration in free quinolinium ion solutions can be satisfactorily explained by the inner filter effect. An alternative explanation in terms of the Stern-Volmer equation⁶⁴, due to self-quenching is not easy to eliminate since there is some doubt as to whether the intercept in figure 3.6 at $[\text{quH}^+]_0 = 0$ is finite. If the intercept is zero then the inner filter model applies; if it is finite then a self-quenching explanation is also applicable.

It seems more reasonable that the inner filter effect is wholly responsible for the fall in the observed fluorescence intensity in quinoline-free solutions, since there is no significant deviation for the deuterated ion or in water-doped solutions.

If we define I_R as the actual fluorescence intensity (i.e. after any quenching, and excluding inner filter effects) initiated by I_a , due to total absorption of the incident beam by quinolinium ions alone then for

quinoline-free solutions, from equation 3.12:

$$I_R^0 = I_c = \ell \cdot \epsilon'_{quH^+} [quH^+]_0 I_F \quad 3.19$$

Experimentally we find (equation 3.7) $[quH^+]_0 \cdot I_F = 4.10$, hence

$$\epsilon'_{quH^+} = 0.244 I_R^0$$

For mixed solutions an adjustment must be made to allow for absorption of I_a by free quinoline (equation 3.8).

$$I_R = \frac{I_c \cdot \sum [x_i]_0 \epsilon_i}{\epsilon_{quH^+} [quH^+]_0} \quad 3.20$$

Then equation 3.12 gives

$$I_R = \frac{\ell \sum [x_i]_0 \epsilon'_i \cdot \sum [x_i]_0 \epsilon_i}{\epsilon_{quH^+} [quH^+]_0} I_F \quad 3.21$$

which effectively differs from equation 3.13 only in that I_R is variable, due to quenching of fluorescence, whereas B was a constant..

Now, if $(\epsilon'_{qu}/\epsilon'_{quH^+}) = \beta$, then

$$\frac{I_R}{I_R^0} = \frac{0.244 \ell (\epsilon_{qu} [qu]_0 + \epsilon_{quH^+} [quH^+]_0) (\beta [qu]_0 + [quH^+]_0) I_F}{\epsilon_{quH^+} [quH^+]_0} \quad 3.22$$

Suppose $\beta [qu]_0 \ll [quH^+]_0$ and similarly $\epsilon_{qu} [qu]_0 \ll \epsilon_{quH^+} [quH^+]_0$, then:

$$\frac{I_R}{I_R^0} = .244 \ell [quH^+]_0 I_F \quad 3.23$$

And since the experimental results give (figure 3.7, table 3.2)

$$\frac{1}{I_F} = C[qu]_0 + 0.244 [quH^+]_0 \quad 3.24$$

$$\frac{I_R^0}{I_R} = \frac{C[qu]_0}{.244 [quH^+]_0} + 1 \quad 3.25$$

The intercepts given in table 3.2 do not entirely agree with equation 3.7, although the results of that equation are all within the error limits shown. For the purposes of these calculations the values from equation 3.7 have been used. Plots of equation 3.25 are shown in figure 3.9.

3.3.3 The Nature of the Quenching Process

The evidence of figure 3.9 indicates that the fluorescence of the quinolinium ion is truly quenched by the addition of quinoline base. It is clear that this cannot be due to a static quenching by complex formation, in which only free quinolinium ions fluoresce, since the slopes are much too steep for this mechanism. For example a value of $I_R^0/I_R = 10$ would imply that 90% of the ions were complexed, for which there is insufficient base present.

The alternative quenching process is dynamic and takes place through the hydrogen bonded complex as shown

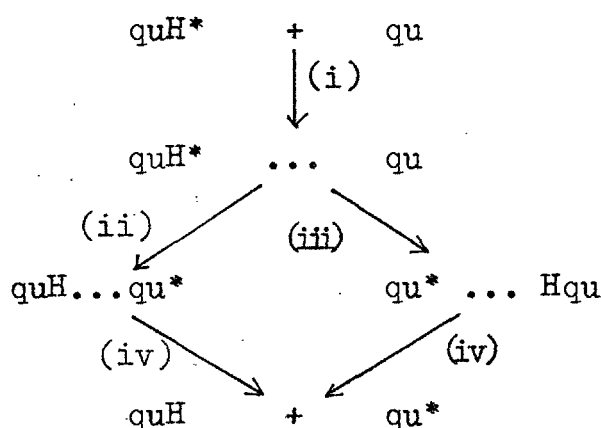


Figure 3.10. The dynamic quenching mechanism.

in figure 3.10. Experimentally, figure 3.9 shows that increasing the total quinoline concentration or decreasing

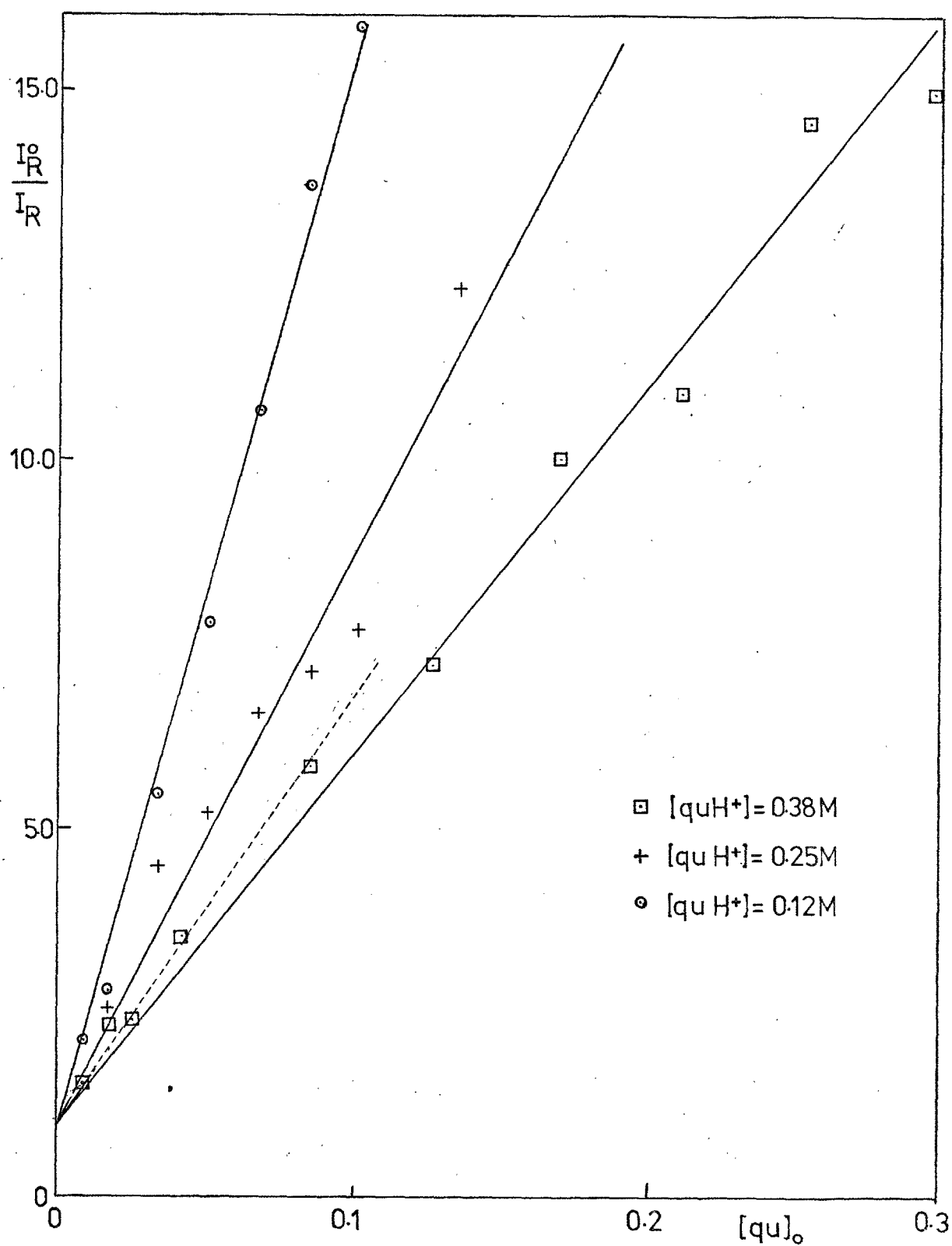


Figure 3.9. The quenching of quinolinium fluorescence by added quinoline.

the total quinolinium concentration increases the quenching. The same trends increase the fraction of ions complexed.

For each point on one line in figure 3.9 the number of excited ions is the same. If the gradient of each line is multiplied by $[quH]_0$, the results are approximately equal. This gives the quenching effect upon a constant population of excited quinolinium ions.

The rate determining step in figure 3.10 is reaction (i) and the rate of the scheme is therefore proportional to $[qu]_0$ for a constant population $[quH^*]$. The quenching of fluorescence observed may be accounted for by the reaction scheme in figure 3.10.

It is of interest to consider the nature of the quenching step. Since excited quinoline base undergoes rapid conversion to the triplet ($n \pi^*$) state it does not fluoresce. Therefore there are two mechanisms open to consideration. Either the excited proton donor loses the proton in the complex, (iii), or there is exciton transfer across the hydrogen bond, (ii). The lowest excited state in quinolinium is ($\pi \pi^*$), which increases the basicity of the quinoline nitrogen compared to the ground state. It would therefore be expected that process (iii) should be difficult since the proton potential is made asymmetrical by the change in base strength. On the other hand the small degree of overlap, demonstrated in section 3.2.2, between the π -systems of the two bases could be sufficient to allow process (iv). Subsequent breaking of the complex and intersystem crossing in the quinoline completes the quenching process.

The high degree of quenching displayed shows that the process described must occur a number of times during the fluorescence lifetime. It would be of interest therefore to carry out time resolved experiments in an attempt, not only to measure the fluorescence of the quinolinium ions, but also to detect phosphorescence of the base molecules following transfer of excitation.

CHAPTER 4.

4. LOW TEMPERATURE INFRA-RED STUDIES OF THE COMPLEX CATION $(\text{py}_2\text{H})^+$, 1700-600 cm^{-1} .

4.1 Introduction

The general conclusion drawn from the evidence of the infra-red spectra of symmetric and asymmetric complexes between nitrogen heterocyclic bases and their conjugate acids is that, even in symmetric complexes the proton is, on the infra-red time-scale, located asymmetrically. The rejection of the symmetric single minimum on the grounds that the symmetric N-N stretch (ν_σ) would be infra-red inactive has been made already¹². A general rejection of single minimum potentials in NHN hydrogen-bonds can also be made since the N-N distance (around 2.8 Å) is considered to be too long²¹. A high barrier double minimum potential is a feasible alternative, because the tunnelling rate would be very slow compared to the infra-red time-scale - effectively trapping the proton in one well. The principal evidence against this model comes from the two imidazole complexes whose crystal structures have been solved^{31,65}. The proton in these complexes was unambiguously observed on one side of the bond - a fact attributed to the crystal field - and the marked similarities between the infra-red spectra of the complex in the crystal and in solution suggest a similar proton potential in solution^{21,44}.

In solution, as already discussed, continuous molecular fluctuation leads to an averaging of the polarization which results in a long-term symmetry in the proton potential (Section 1.4, figure 1.2). Crystallisation of complexes therefore has a particular value since the proton may be permanently fixed in an asymmetric potential. Unfortunately complexes of pyridine bases (as opposed to imidazole bases) have generally proved unamenable to crystallisation, although evidence for one such complex is presented elsewhere in this work.

An alternative method of producing solid samples for infra-red examination is to freeze solutions containing complexes rapidly to liquid nitrogen temperatures. In this way, it is to be hoped, the individual components will not separate, and the complex will be trapped in a fixed field. This is the technique used in the work described in this chapter.

Previous low temperature studies⁶⁶ upon the complex $(\text{py}_2\text{H})^+$ have covered the N-H stretching region, although a few measurements were made upon the ν_{6a} (ring-elongation) band. In that work pyridinium salts were dissolved in excess free base. Foglizzo and Novak⁶⁷ have studied the crystalline pyridinium halides at room and liquid nitrogen temperatures, but only in the 4000-1500 and 300-20 cm^{-1} ranges. The infra-red spectrum 4000-200 cm^{-1} , of pyridine has also been investigated⁶⁸ down to 5K.

4.2 The Solutions Examined

1.0M solutions of pyridine and of pyridinium salts in acetonitrile were examined with and without the

addition of an 0.25M quantity of the second component. Use of pairs of solutions, each with one component in excess, has several advantages over other methods. It is hoped that the minor constituent will be completely complexed (evidence for this can be obtained by the certain absence of bands at frequencies characteristic of that constituent). Almost the entire spectrum may be examined without interference by bands of the two free components, by comparison between solutions with each component in excess. The effective environment is altered when the major constituent is changed; excess pyridinium salt gives a more ionic sample.

Two counter-ions were used - fluoroborate and hexafluorophosphate - and the effect of the variation upon the spectra examined. Both acetonitrile and trideutero-acetonitrile were used as solvents in order that the entire spectrum might be examined without interference from solvent absorption. This method has the additional advantage that each solute combination was examined twice with a consequent check upon the reproducibility of freezing. The deuterium bridged complex, $(\text{py}_2\text{D})^+$, was also examined with both counter-ions, but only in trideutero-acetonitrile.

The combinations described above gave rise to twenty samples. The spectra obtained are presented in appendix 2, in an arrangement designed to aid simple comparison between them. Individual sections of spectra to illustrate points in the discussion are provided where appropriate in the text.

4.3 The Nature of the frozen state

The first important fact to be established is the nature of the sample in the frozen state. Firstly it may be stated that in all mixed solutions the minor constituent is fully complexed. The evidence for this is in each case the definite absence of at least one band characteristic of the minor constituent. As a result all bands observed in the spectrum must be assigned to the solvent, major constituent, counter-ion or complex. The absence of free pyridinium salt bands when it is the minor constituent also indicates that freezing was sufficiently rapid to prevent precipitation.

There are marked differences between the spectra of samples containing different counter-ions. Fluoroborate samples give rise to broader bands than fluorophosphate samples. In addition the peaks in spectra of the latter are often split where pyridinium ions are in excess. This suggests that crystallisation has occurred in the fluorophosphate system and that lattice splitting can be observed in samples containing excess salt, whereas the fluoroborate samples are amorphous. An example of this effect is observed in figure 4.2 at about 680 cm^{-1} . In table 4.3 the splitting is clearly indicated. In some modes there is an apparent frequency shift between fluoroborate and fluorophosphate samples. This can be ascribed to lattice splitting in which one of the two components is obscured.

There is no substantial difference between the spectra of solutions in acetonitrile and in trideutero-acetonitrile, except for solvent absorption bands.

This is taken to indicate a satisfactory consistency in the method of treating the samples.

4.4 Identification of bands due to complex species

The most significant object of this work is to detect pairs of frequencies characteristic of a single internal mode. This is the single most important area of study which prevents certain identification of the instantaneous asymmetric potential in solution. A systematic search through the spectra presented in appendix 2 reveals a large number of frequencies which cannot be assigned to the solvent, counter-ion or major component of the solution. Of these frequencies, the majority are observed only in one member of a pair of samples (i.e. in the excess salt sample but not in the excess base sample or vice versa), because the frequency of absorption is obscured in the other member by absorption due to the excess component (type-f bands). A small class of frequencies comprises those which are observed in one member and are clearly absent in the other (type-g bands). This class includes some frequencies assigned to modes which are split in samples containing excess fluorophosphate salt. A final class contains frequencies at which bands are observed in both members of a given pair of solutions (type-h bands). The results of the search and the tripartite classification are shown for $(py_2H)^+$ in table 4.1, and for $(py_2D)^+$ in table 4.2.

TABLE 4.1 Frequencies (in cm^{-1}) of bands observed in the low temperature spectra, assigned to the $(\text{py}_2\text{H})^+$ complex.

BF_4^- COUNTER-ION				PF_6^- COUNTER-ION			
in CH_3CN		in CD_3CN		in CH_3CN		in CD_3CN	
excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>
-	-	-	-	-	-	1663 h	1663 h
1640 f	-	1639 f	-	1640 f	-	1640 f	-
-	-	-	-	1604 f	-	1604 f	-
-	-	-	-	-	1595 f	-	1595 f
-	-	-	-	-	1562 f	-	1561 g
1547 f	-	1550 f	-	-	1552 f	-	-
1486 f	-	1486 f	-	1488 f	-	1488 f	-
-	-	-	1442 f	-	-	1452 h	1445 h
-	-	1405 h	1413 h	-	-	1406 h	1410 h
1282 f	-	-	-	-	-	-	-
1257 h	1256 h	-	-	1258 h	1263 h	-	-
-	-	-	-	1233 g	-	-	-
1217 g	-	-	-	1217 g	-	-	-
-	-	-	-	-	1213 f	-	-

Continued

TABLE 4.1 (CONTINUED) : 2

BF ₄ ⁻ COUNTER-ION				PF ₆ ⁻ COUNTER-ION			
in CH ₃ CN		in CD ₃ CN		in CH ₃ CN		in CD ₃ CN	
excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>
1204 g	-	-	-	1205 f	-	-	-
-	-	-	-	1164 f	-	-	-
-	-	-	-	1156 h	1154 h	1157 h	1158 h
1150 g	-	1147 g	-	-	-	-	-
-	-	-	-	1110 h	1110 h	-	-
-	-	-	-	1073 h	1073 h	1072 h	1073 h
-	-	-	-	-	1046 f	-	-
1005 f	-	1007 f	-	1008 f	-	1008 f	-
-	-	-	-	-	991 f	-	991 f
-	957 f	-	956 f	957 g	-	957 h	957 h
-	-	-	892 g	-	-	-	-
-	-	-	-	-	-	780 h	781 h
-	-	-	772 f	-	767 g	-	767 g
-	-	765 f	-	765 f	-	764 g	-
-	-	-	-	762 f	-	761 h	761 h
-	-	-	-	-	759 f	-	-

Continued../3

TABLE 4.1 (CONTINUED) : 3

BF ₄ ⁻ COUNTER-ION				PF ₆ ⁻ COUNTER-ION			
in CH ₃ CN		in CD ₃ CN		in CH ₃ CN		in CD ₃ CN	
<u>excess</u> <u>base</u>	<u>excess</u> <u>salt</u>	<u>excess</u> <u>base</u>	<u>excess</u> <u>salt</u>	<u>excess</u> <u>base</u>	<u>excess</u> <u>salt</u>	<u>excess</u> <u>base</u>	<u>excess</u> <u>salt</u>
-	-	-	-	758 g	-	757 h	757 h
-	-	-	-	-	754 f	-	752 f
-	703 f	-	701 f	-	703 f	-	702 f
-	-	-	-	-	699 g	-	698 g
-	-	-	696 f	-	-	-	-
688 f	-	688 f	-	-	-	-	-
-	-	-	-	-	687 g	-	686 f
-	-	-	-	684 g	-	684 h	684 h
-	-	-	-	-	680 g	-	680 f
-	-	-	-	636 g	-	636 g	-
-	-	-	-	-	632 g	-	632 g
630 h	631 h	630 h	631 h	-	-	630 g	-
-	-	-	-	-	595 g	-	593 g

f : band observed in either excess base or excess salt samples which might be observed in the other member of the pair if the region were not obscured by other features.

g : band observed in either excess base or excess salt which is clearly absent in the other member of the pair.

h : band which is clearly observed in both members of the pair.

Principal regions in which interference occurs are 1470-1350, 1050-1020, 917 and 773 cm⁻¹ (CH₃CN); 1300-1000, 860-820 and 730-700 cm⁻¹ (CD₃CN); 1150-990 cm⁻¹ (BF₄⁻); 940-790 cm⁻¹ (PF₆⁻).

TABLE 4.2 Frequencies (in cm^{-1}) of bands observed in the low temperature spectra, assigned to the $(\text{py}_2\text{D})^+$ complex.

BF_4^- COUNTER-ION		PF_6^- COUNTER-ION	
in CD_3CN		in CD_3CN	
<u>excess base</u>	<u>excess salt</u>	<u>excess base</u>	<u>excess salt</u>
-	-	-	1689 g
-	-	1665 g	-
-	-	1604 f	-
-	1597 f	-	1600 f
-	-	-	1575 g
1490 f	-	1490 f	-
-	-	1487 f	-
1483 f	-	-	-
-	1448 f	1449 h	1448 h
-	-	-	1445 g
-	-	-	1279 g
-	1265 f	-	-
-	-	1220 g	-
-	-	1157 h	1155 h
1148 g	-	-	-
-	-	1072 h	1074 h
1004 f	-	1008 f	-
-	-	-	969 g
-	937 g	-	-
-	764 g	764 h	764 h
-	762 g	761 f	-
-	-	757 f	-
-	-	746 h	746 h
-	-	-	741 g
-	-	-	736 g
-	-	-	699 g
-	693 g	-	-
688 h	687 h	-	-
-	-	-	686 g
-	-	683 g	-
-	-	-	669 g

(continued)

TABLE 4.2 (continued) : 2

BF ₄ ⁻ COUNTER-ION		PF ₆ ⁻ COUNTER-ION	
in CD ₃ CN		in CD ₃ CN	
excess <u>base</u>	excess <u>salt</u>	excess <u>base</u>	excess <u>salt</u>
-	-	635 f	-
-	-	631 f	-
627 h	629 h	-	-
-	-	-	589 g
-	-	564 g	-

The letters f, g and h have the same meaning as in Table 4.1.

4.5 Assignment of frequencies to specific internal modes

The assignment of the bands in the low temperature spectra has been carried out following the room temperature assignment of Clements and Wood^{66,69}. The notation used to identify the internal modes is the same as that used by Clements and Wood and is due to Green, Kynaston and Paisley⁷⁰. A summary of the assignments is presented in tables 4.3 and 4.4. Consideration will first be given to three regions in which observations of particular interest have been made. In the following sections the terms "salt-like" and "base-like" are used to distinguish vibrations of the donor and acceptor rings respectively.

TABLE 4.3 The Assignment of Frequencies (in cm^{-1}) from the Low Temperature Spectra of the complex, $(\text{py}_2\text{H})^+$.

ROOM TEMPERATURE ⁶⁹				LOW TEMPERATURE				
	<u>Base</u>	<u>Salt</u>	<u>Complex</u>	<u>Base</u>	<u>Salt</u>	<u>Base-like</u>	<u>Complex</u>	<u>Salt-like</u>
ν_{8a}	1583	1640	1639	1578	1638	(1595)		1640
ν_{8b}	1572	1612	1603	1568	$\left\{ \begin{array}{l} 1613(\text{BF}_4) \\ 1606(\text{PF}_6) \end{array} \right\}$	1595		1604
ν_{19a}	1482	1542	1549	1477	1535	1488?		$\left\{ \begin{array}{l} 1562 \\ 1552 \end{array} \right\} (\text{PF}_6)$
								1550(BF_4)
ν_{19b}	1439	1490	1493	1432	1490	1452—1445		1488
ν_{14}	1375	(1379)			1376		1406	
ν_3		1332			1333		1282(BF_4)	
ν_{9b}		1255	1255		$\left\{ \begin{array}{l} 1260(\text{BF}_4) \\ 1253(\text{PF}_6) \end{array} \right\}$		1258—1263	
ν_{9a}	1218	1207	1205		1206	1217—1213		1205
ν_{15}	1148	1174	1167	1139	1167	1156		1164
ν_{18a}	1068	1050	1040	1063	1056	1073		1046

(Continued)

TABLE 4.3 Continued : 2

ROOM TEMPERATURE ⁶⁹				LOW TEMPERATURE				
	<u>Base</u>	<u>Salt</u>	<u>Complex</u>	<u>Base</u>	<u>Salt</u>	<u>Base-like</u>	<u>Complex</u>	<u>Salt-like</u>
ν_1	993	997	1007	990		991		1008
δ_{NH}		948(R)	948					957
ν_{10a}	886	(883)			883		892	
ν_{10b}		(895)	762?	(751)		780		
ν_4	749	748		751	$\left\{ \begin{array}{l} 752(\text{BF}_4) \\ 747(\text{PF}_6) \end{array} \right\}$	$764\text{---}767$ $761\text{---}761$	$(\text{PF}_6) \longleftrightarrow ?$	$757 < \begin{array}{l} 757 \\ 752 \end{array}$
ν_{11}	703	675	684	706	676	$\left\{ \begin{array}{l} 703(\text{BF}_4) \\ 703(\text{PF}_6) \\ 699 \end{array} \right\}$		$688(\text{BF}_4)$ $684 < \begin{array}{l} 687(\text{PF}_6) \\ 680 \end{array}$
ν_{6a}	605	610	628	603	610	$\left\{ \begin{array}{l} 636\text{---}632(\text{PF}_6) \\ 630(\text{BF}_4) \end{array} \right\}$		

TABLE 4.4 The Assignment of Frequencies (in cm^{-1}) from the Low Temperature Spectra of the complex, $(\text{py}_2\text{D})^+$.

ROOM TEMPERATURE				LOW TEMPERATURE				
	<u>Base</u>	<u>Salt</u>	<u>Complex</u>	<u>Base</u>	<u>Salt</u>	<u>Base-like</u>	<u>Complex</u>	<u>Salt-like</u>
ν_{8a}	1583	1639	1637	1578	1634			
ν_{8b}	1572	1590	1600	1568	1585	1575		1600
ν_{19a}	1482	1488		1477	1491	1483		1487
								$\updownarrow$?
ν_{19b}	1439	1490	1540	1432	1491	1449	1448 1445	1490
ν_{14}	1375	(1370)				$\left\{ \begin{array}{l} 1279(\text{PF}_6) \\ 1265(\text{BF}_4) \end{array} \right\}$		
ν_3		1305			1303			
ν_{9b}		930			945			
ν_{9a}	1218	1205	1206			1220		
ν_{15}	1148	1172	1170	1139	1167	1156		
ν_{18a}	1068	1050	1037	1063		1072		

(Continued)

TABLE 4.4 (Continued) : 2

	ROOM TEMPERATURE			LOW TEMPERATURE				
	<u>Base</u>	<u>Salt</u>	<u>Complex</u>	<u>Base</u>	<u>Salt</u>	<u>Base-like</u>	<u>Complex</u>	<u>Salt-like</u>
ν_1	993	(996)	1005	990				1004(BF ₄) 1008(PF ₆)
γ_{NH}		797						
ν_{10a}	886	(880)			884			
ν_{10b}			762?	(751)				
ν_4	749	680		751	682	< 764 762		746 < 746 741
ν_{11}	703	659	684	706	$\begin{Bmatrix} 647 \\ 634 \end{Bmatrix}$ (BF ₄) $\begin{Bmatrix} 637 \\ 631 \end{Bmatrix}$ (PF ₆)	704(BF ₄) 699(PF ₆)		689 < 693 687 (BF ₄) 686 (PF ₆) 683
ν_{6a}	605	603	625	603	603	635 > (PF ₆) 631		
						628(BF ₄)		

4.5.1 The 780-630 cm^{-1} region

In room temperature spectra the ν_{11} and ν_4 bands occur in this region. In the complex $(\text{py}_2\text{H})^+$ the two sets of bands are well separated and may be considered separately. The spectra of this region for the $(\text{py}_2\text{H})^+$ are shown in figures 4.1 (fluoroborate) and 4.2 (fluorophosphate).

In the fluoroborate it is clear that two distinct $(\text{py}_2\text{H})^+ \nu_{11}$ bands are observed at 688 and 703 cm^{-1} . Both are type-f bands and we should expect that the free moiety ν_{11} bands are concealing the second component in each spectrum. In the fluorophosphate spectra, the characteristic splitting due to crystallisation discussed in section 4.3 may be observed. In excess salt the sharp salt-like band observed at 684 cm^{-1} in excess base has split into a doublet at 680 and 687 cm^{-1} . The base-like component is only observed in excess salt; it is a doublet at 699 and 703 cm^{-1} .

The $(\text{py}_2\text{H})^+ \nu_4$ bands are between 770 and 750 cm^{-1} . The frequencies of the free moiety bands are very close together so that it is difficult to disentangle any new features due to the complex. A fluoroborate counter-ion band at 767 cm^{-1} also obscures part of this region. A number of new features in the fluorophosphate solution (figure 4.2) may be distinguished. The 757 cm^{-1} band in excess base solutions splits in excess salt solutions to give two bands at 752 and 757 cm^{-1} . However there appears to be a correspondence between the two bands in excess base (761 and 764 cm^{-1}) and two bands in excess salt

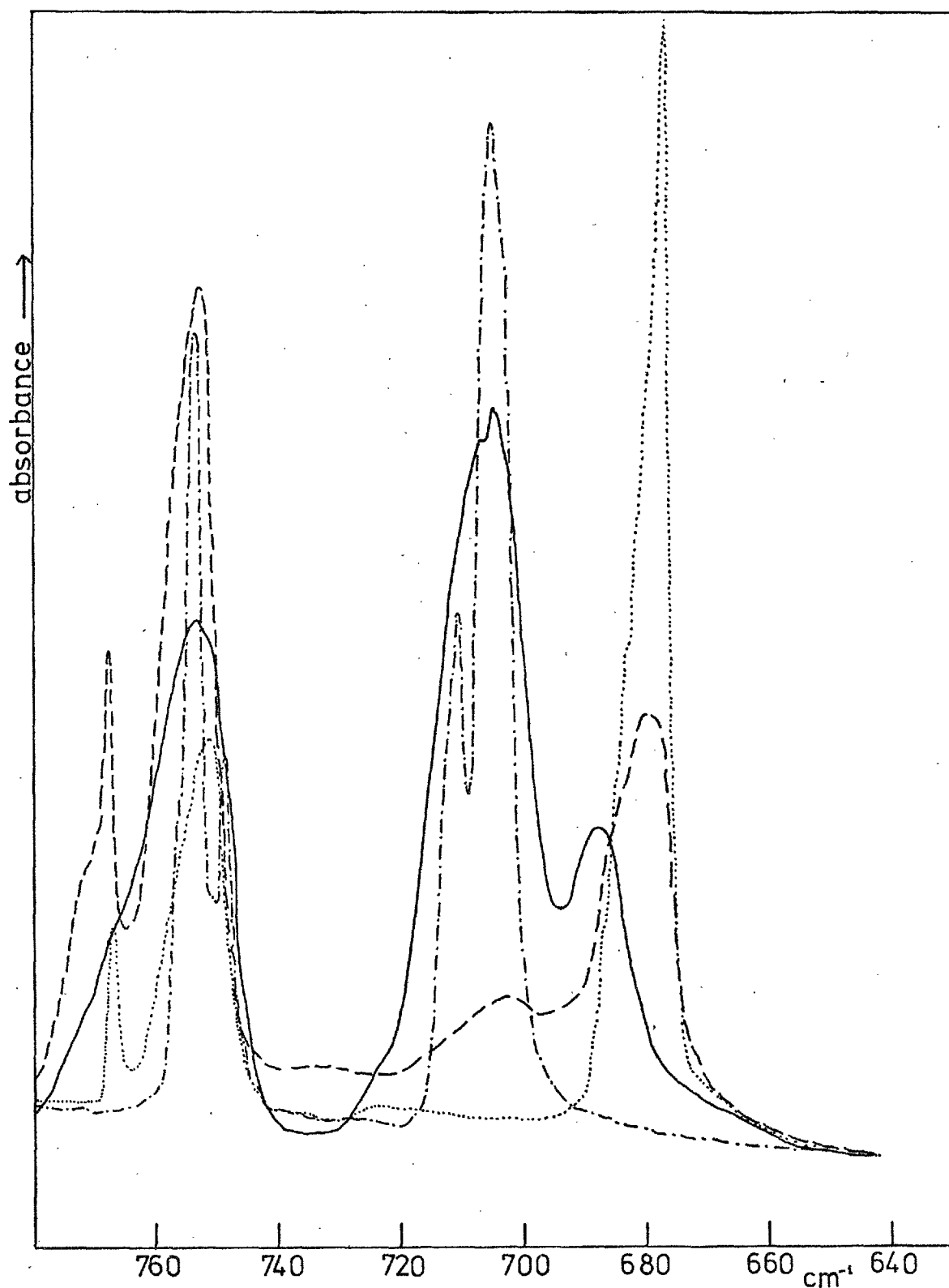


Figure 4.1. Low temperature infra-red spectrum of $(\text{py}_2\text{H})^+$, $780\text{--}630\text{ cm}^{-1}$. $780\text{--}730\text{ cm}^{-1}$ in CD_3CN , $730\text{--}630\text{ cm}^{-1}$ in CH_3CN . (.....: salt, ----: base, ---: excess salt, —: excess base). BF_4^- counter-ion.

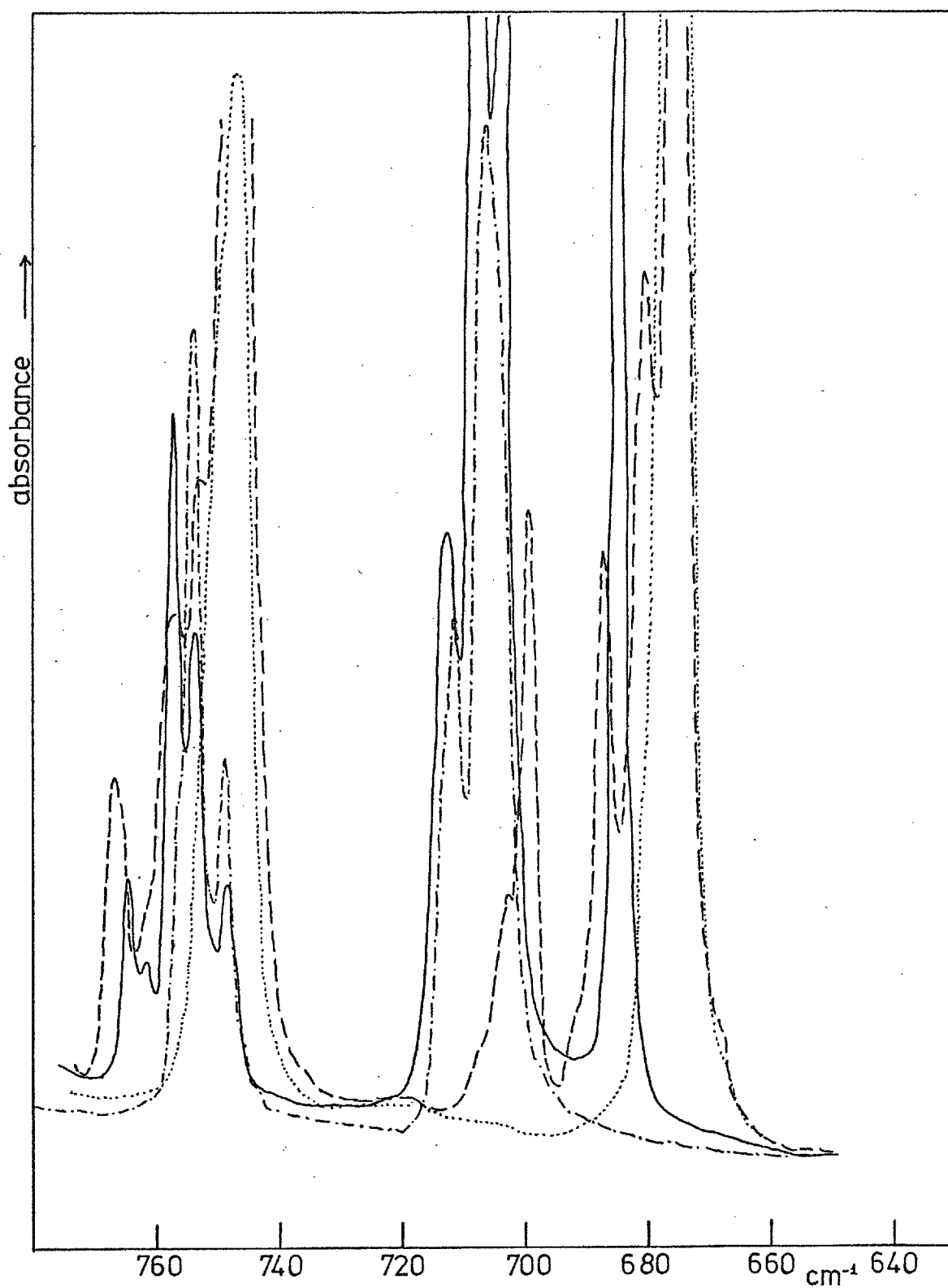


Figure 4.2. As figure 4.1 but PF_6^- counter-ion.

solution at 761 and 767 cm^{-1} . No distinction between salt-like and base-like complex bands can be made in this case.

Upon deuteration the frequency of the free salt ν_4 mode falls to 682 cm^{-1} and that of the ν_{11} mode to about 640 cm^{-1} . The position of the latter appears to be counter-ion dependent at low temperatures as its upper and larger component occurs at 647 cm^{-1} in the fluoroborate and at 637 cm^{-1} in the fluorophosphate. In each case there is a smaller peak (at 634 and 631 cm^{-1} respectively). Figures 4.3 and 4.4 show the spectra of the deuterated system.

The appearance of the region 720-680 cm^{-1} in the spectrum of the deuterated fluoroborate system (figure 4.3) is broadly similar to that of the protonated system (figure 4.1). However if these two new frequencies (689 and 704 cm^{-1}) are assigned to ν_{11} as in the protonated system then the assignment of bands to ν_4 is more difficult, because these two bands are lying almost on top of the free salt ν_4 band. In fluorophosphate solutions (figure 4.4) the 689 cm^{-1} band is sharpened and shifted to 683 (excess base) or 686 cm^{-1} (excess salt). The free $\text{pyD}^+\text{PF}_6^-$ ν_4 mode exhibits a doublet, 682 and 687 cm^{-1} , with both components of equal intensity. In the excess salt sample the 687 cm^{-1} component increases in intensity whilst the 682 cm^{-1} component decreases; the former, it is assumed, is enhanced by complex absorption which must, by this assignment, be ν_{11} . The base-like $(\text{py}_2\text{D})^+$ band in fluorophosphate is sharpened and shifted to 699 cm^{-1} .

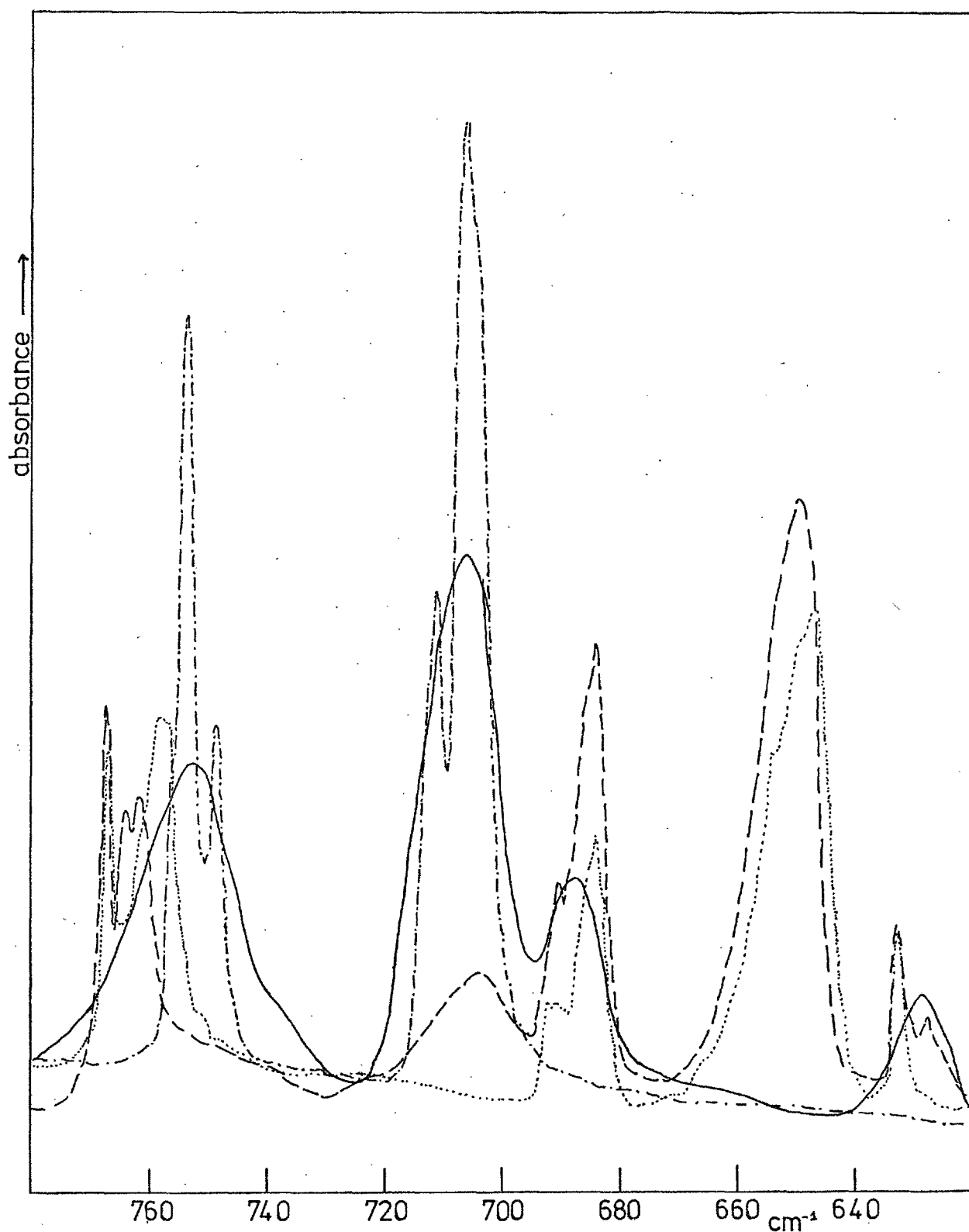


Figure 4.3. Low temperature infra-red spectrum of $(py_2D)^+$, 780-620 cm^{-1} . Entire range of salt spectrum run in CD_3CN , otherwise as figure 4.1. BF_4^- counter-ion.

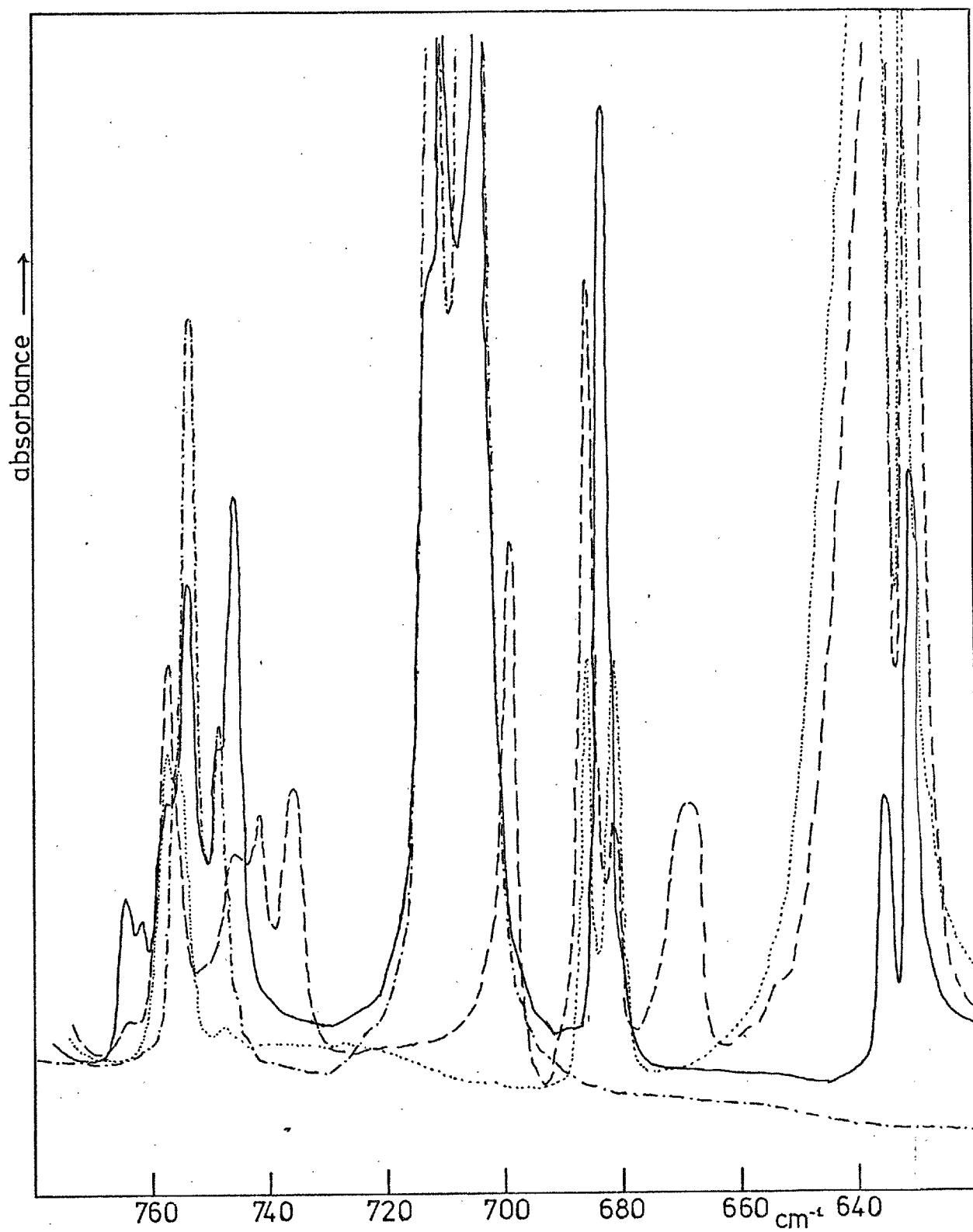


Figure 4.4. As figure 4.3 but all samples in CD_3CN , PF_6^- counter-ion.

A similar problem arises in the region of the free deuterated salt ν_{11} band. In the fluoroborate the ν_{6a} assignment at 628 cm^{-1} is clear of the lower component of free salt ν_{11} . However in the fluorophosphate it is necessary to assign two new bands in excess base ($635, 631\text{ cm}^{-1}$) to the ν_{6a} mode, even though they are right under the free salt ν_{11} band.

Since the free base bands are unmoved by deuteration, the ν_4 region of interest still extends to 770 cm^{-1} . In the fluoroborate incipient splitting (762 and 764 cm^{-1}) may be assigned to the base-like component - compared to 765 and 772 in the protonated case. Five new frequencies can be found in the fluorophosphate spectrum. Two, at 761 and 764 cm^{-1} , correspond to those observed in fluoroborate; two are g-type bands and one is an h-type band. If some of these are to be classified as ν_4 salt-like frequencies then they are a particularly long way from the free salt band (682 cm^{-1}), but close to the frequencies of the protonated complex. This suggests that deuteration is not an important factor in determining the frequency of ν_4 bands. Clements and Wood⁶⁹ assign no frequency to either the protonated or deuterated complex ν_4 band at room temperature.

4.5.2 The $1570\text{--}1430\text{ cm}^{-1}$ region

This is the region of the modes ν_{19a} and ν_{19b} . There is a certain amount of disagreement in the literature as to which band is assigned to each mode in the pyridinium ion. Clements,⁶⁶ room temperature assignment is used

here and is shown in table 4.3. The alternative assignment of Cook⁷¹ and of Foglizzo and Novak^{67,72} requires the frequency of ν_{19b} to shift from 1439 to 1542 cm^{-1} upon protonation. Furthermore the two bands assigned here to ν_{19a} are less intense than their ν_{19b} counterparts.

Figures 4.5 and 4.6 show the spectra of the $(\text{py}_2\text{H})^+$ fluoroborate and fluorophosphate samples respectively between 1700 and 1350 cm^{-1} . In the fluoroborate a pair of f-type bands at 1442 and 1486 cm^{-1} may be assigned to the base- and salt-like ν_{19b} modes respectively. In the fluorophosphate excess base sample both these bands may be observed at 1452 and 1488 cm^{-1} . The former band shifts to 1445 cm^{-1} in the excess salt sample and may show the splitting due to crystallisation discussed earlier.

The strength of the free base and free salt ν_{19b} bands assists in the necessary conclusion that all the minor constituent is complexed in the mixed samples. The free base band at 1432 cm^{-1} is clearly absent in both excess salt samples (figures 4.5 and 4.6), whilst the free salt band at 1490 cm^{-1} is absent from the excess base fluorophosphate spectrum.

The ν_{19a} free base band (1477 cm^{-1}) occupies the same region as the ν_{19b} free salt band (1490 cm^{-1}). Therefore there is difficulty in distinguishing the complex bands derived from these two components. Observations of the deuterated complex, $(\text{py}_2\text{D})^+$, do not help with the comparison since the free deuterated salt ν_{19a} band (1491 cm^{-1}) also moves into this region. The band observed at 1488 cm^{-1} in all excess base samples is in all cases of

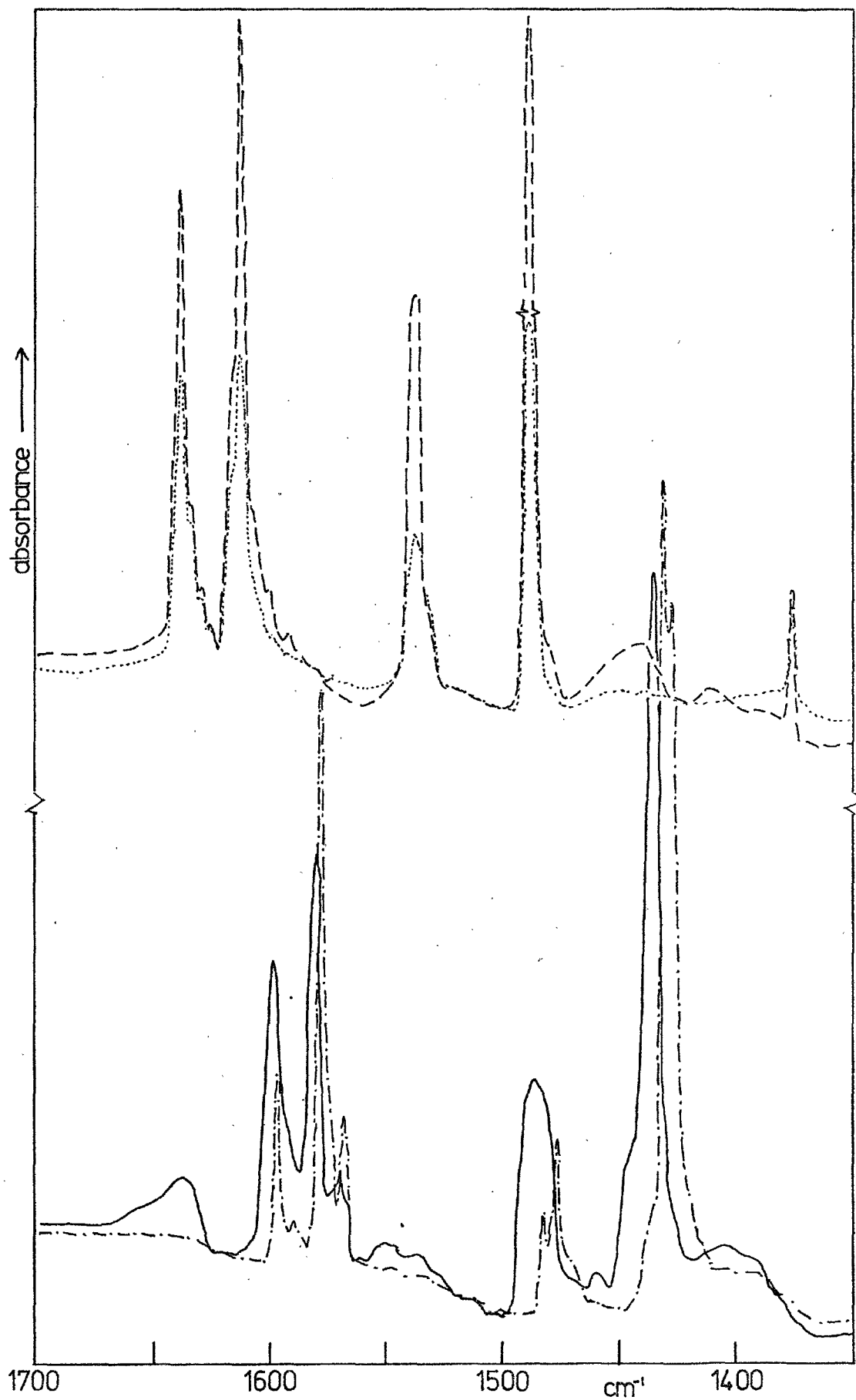


Figure 4.5. Low temperature infra-red spectrum of $(\text{py}_2\text{H})^+$, 1700-1350 cm^{-1} . In CD_3CN , BF_4^- counterion. Lines as in figure 4.1.

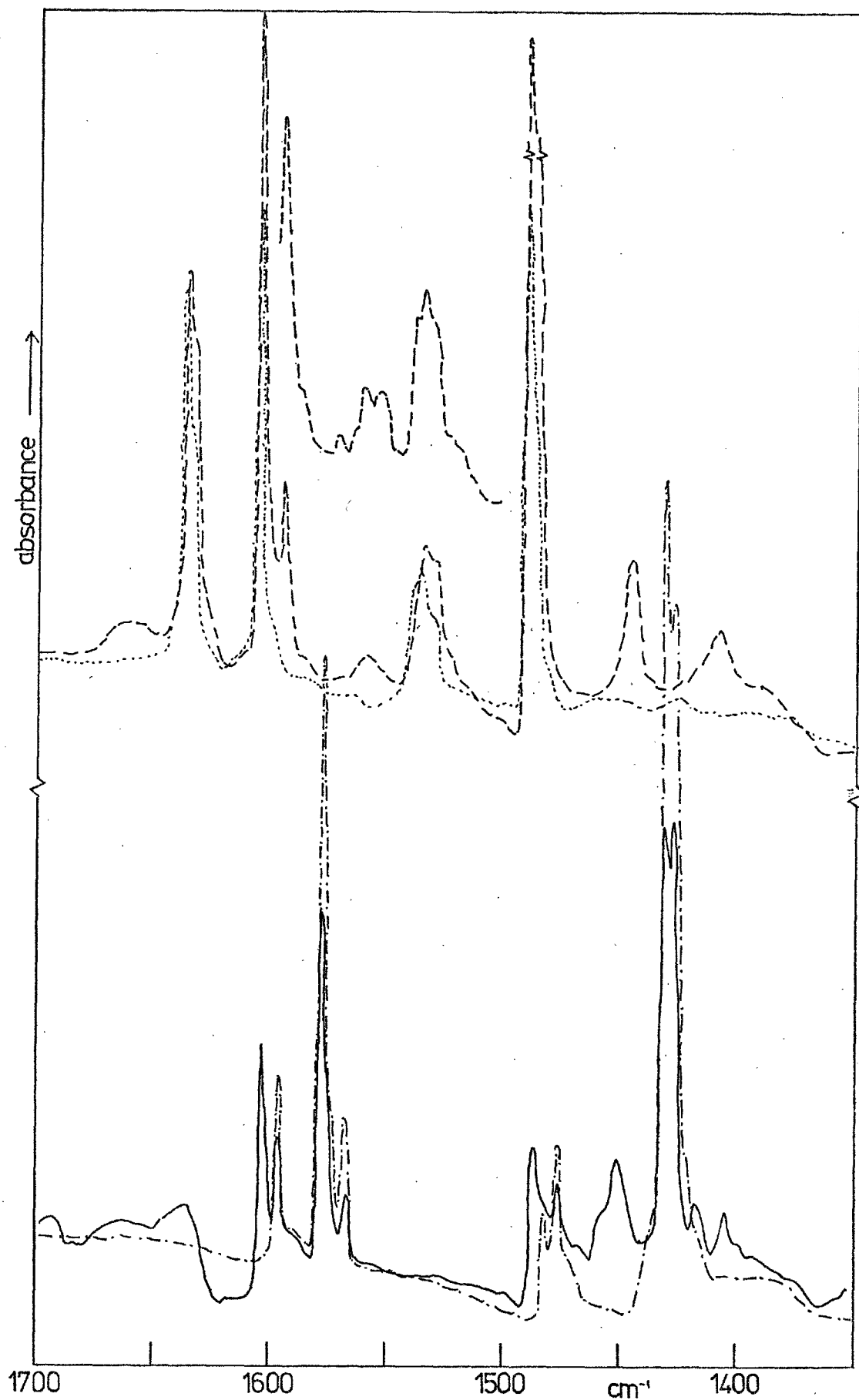


Figure 4.6. As figure 4.5 but PF_6^- counter-ion.
 Inset: 1600-1500 cm^{-1} excess salt
 spectrum in CH_3CN .

the f-type. It is assigned to the salt-like ν_{19b} complex mode but the possibility of the alternative assignment is indicated in table 4.3.

The excess fluorophosphate salt splitting is observed for the salt-like ν_{19a} at 1552 and 1562 cm^{-1} , but only in CH_3CN (figure 4.6, inset). In the fluoroborate there is a single corresponding band at 1550 cm^{-1} .

In the deuterated system, $(\text{py}_2\text{D})^+$ (figures 4.7 and 4.8), there is clear evidence of the base-like bands of both the ν_{19a} and ν_{19b} modes. In ν_{19b} excess salt splitting is observed at 1445 and 1448 cm^{-1} in the fluorophosphate. The corresponding single band in the fluoroborate is at 1448 cm^{-1} . For ν_{19a} the base-like band is observed in excess fluoroborate salt at 1483 cm^{-1} but appears to be obscured in the fluorophosphate sample.

The region of the two salt-like modes (1485-1495 cm^{-1}) shows two bands in the excess base fluorophosphate sample spectrum (figure 4.8). These may be logically assigned to ν_{19a} (1487 cm^{-1}) and ν_{19b} (1490 cm^{-1}) following the data from the room temperature spectra⁶⁹. In the fluoroborate spectrum the 1490 cm^{-1} band appears as a shoulder on the 1483 cm^{-1} band. There may be some dispute over the assignment of this feature in the samples with both counter-ions since there are two alternatives which must be considered. Firstly the shoulders may merely be the effect of noise in the spectrum or secondly the difference in frequency of the bands between the fluoroborate and fluorophosphate samples may be a counter-ion effect. There is a definite sharpening of the

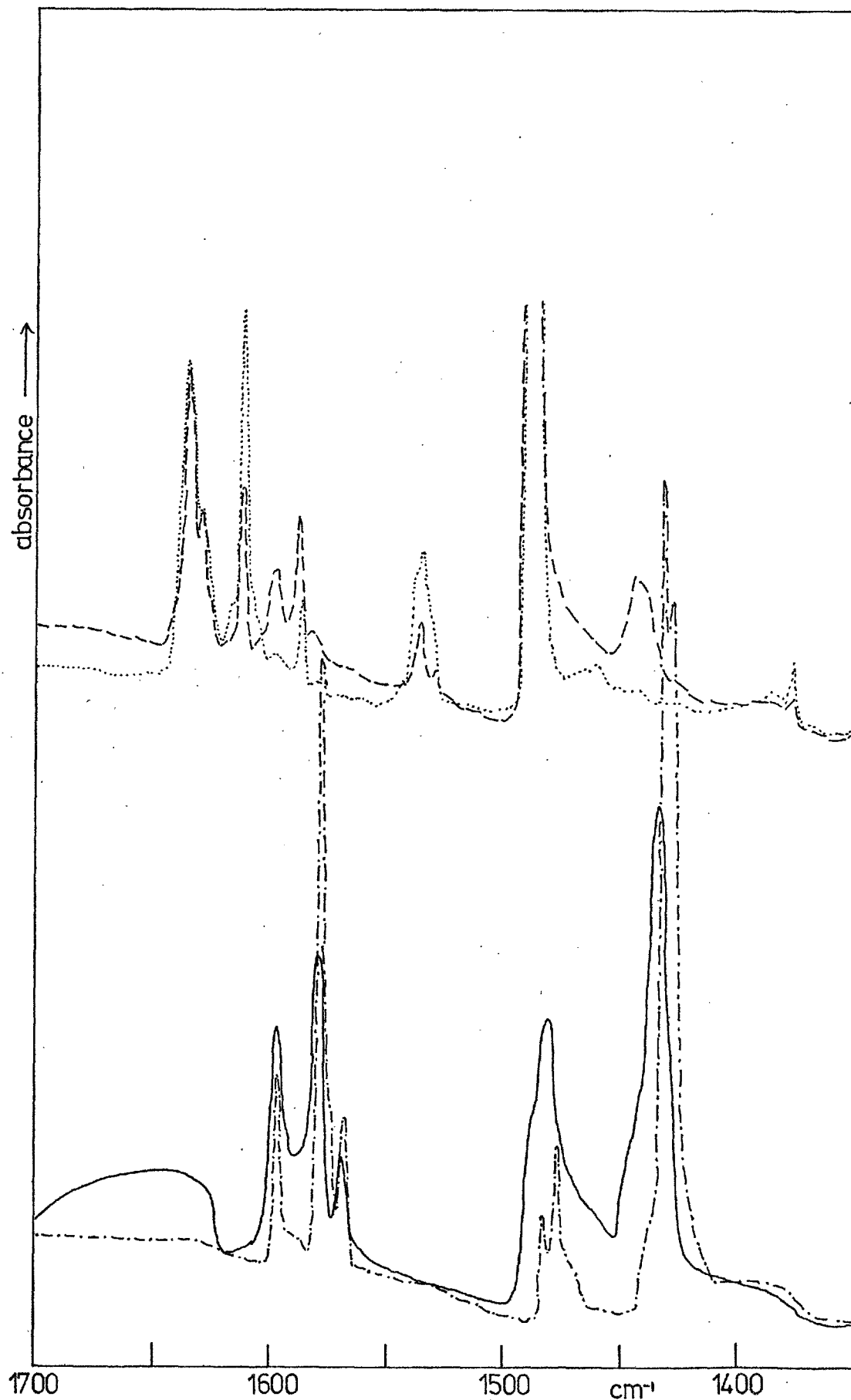


Figure 4.7. Low temperature infra-red spectrum of $(\text{py}_2\text{D})^+$, 1700-1350 cm^{-1} . In CD_3CN , BF_4^- counterion. Lines as in figure 4.1.

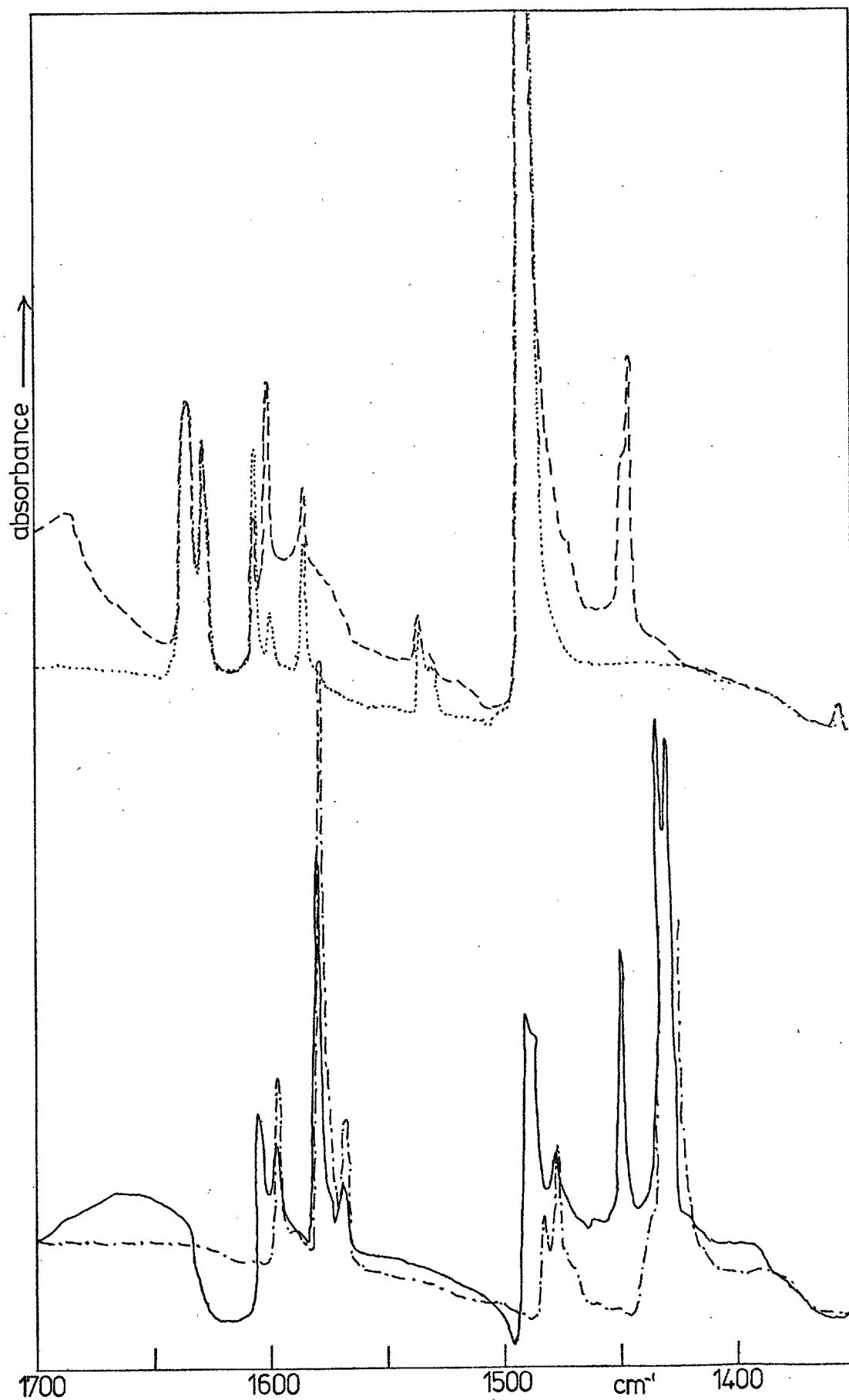


Figure 4.8. As figure 4.7 but PF_6^- counter-ion.

feature in the fluorophosphate sample spectrum. The proposition that the shoulders are distinct features and the difference in frequencies a real effect seems most reasonable and is presented in table 4.4. In that case the effect of varying the counter-ion is clearly seen.

4.5.3 The 1640-1560 cm^{-1} Region

This region in which the ν_{8a} and ν_{8b} modes lie is also presented in figures 4.5-4.8.

There is a pronounced frequency shift for the free salt ν_{8b} band between the fluoroborate (1613 cm^{-1}) and fluorophosphate (1605 cm^{-1}) samples in both free salt and excess salt solutions (and in both CH_3CN and CD_3CN). Other bands due to the free moieties are satisfactorily observed at 1638 cm^{-1} (ν_{8a} , free salt), 1578 cm^{-1} (ν_{8a} , free base) and 1568 cm^{-1} (ν_{8b} , free base). There is a further band of appreciable strength at 1597 cm^{-1} due to free base. It is also observed at room temperature. Corrsin, Fax and Lord⁷³ assign such a frequency to a combination of ν_1 with ν_{6a} .

Two new bands associated with ν_{8b} are observed in mixed solutions at 1595 and 1604 cm^{-1} and can be assigned to the base-like and salt-like modes respectively. The fact that the former appears at the frequency of the overtone mentioned above is not significant since we should expect the complex overtone frequency to be in the region of 1630 cm^{-1} , the ν_{6a} frequency being notably sensitive to complexing.

The ν_{8a} salt-like band is probably that observed at 1640 cm^{-1} . The broadness of this band and the number of possible combination bands at the high frequency end of the region of study introduce an element of doubt. The 1595 cm^{-1} feature assigned to ν_{8b} may possibly be ν_{8a} and this is indicated in table 4.3.

In the deuterated complex, $(\text{py}_2\text{D})^+$, there are a number of candidates for the ν_{8b} mode. These are at 1575 cm^{-1} in the excess fluorophosphate salt sample (which may be assigned to the base-like mode) and around 1600 cm^{-1} in the excess fluoroborate salt and both fluorophosphate samples. It is somewhat surprising that the base-like band moves down 20 cm^{-1} upon deuteration whilst the salt-like band remains almost constant. However the alternative assignment in which the band near 1600 cm^{-1} is always due to the base-like mode leads to a crossing of the modes stemming from each ring upon complexing in both $(\text{py}_2\text{H})^+$ and $(\text{py}_2\text{D})^+$. No other mode of which the base-like frequencies have been assigned shows such a large change upon deuteration but there is no reason for discussing the assignment upon these grounds since, although we would expect salt-like bands to be most sensitive to deuteration, the base-like bands are shifted upon complexing and should therefore be sensitive to the nature of the bridging atom.

No frequencies are assigned to the ν_{8a} mode in the deuterated complex, $(\text{py}_2\text{D})^+$. A broad feature above 1650 cm^{-1} may be the result of some combinations but has not been investigated further.

4.5.4. The Assignment of the Remaining Frequencies

It has proved possible to assign both salt- and base-like frequencies for four further modes (ν_{9a} , ν_{15} , ν_{18a} and ν_1) in the complex $(py_2H)^+$. In all but one case only one band is due to each moiety, and only in one mode has further splitting been detected. Assignment to salt- and base-like features has been facilitated by the similarity in frequencies between complex bands and those of the free moieties. Assignment of various other frequencies has also been made as indicated in tables 4.3 and 4.4.

4.6 Discussion

There is clearly evidence that, for certain vibrational internal modes, bands are observed which are characteristic of the donor and acceptor moieties in the complex. An alternative conclusion, that the observation is merely of frequency shifts due to a variation in the environment, may be rejected on the grounds that in many cases the effect is independent of counter-ion. Although it is evident that the counter-ion has some effect upon the nature of the bands observed it seldom has any influence upon the positions of the complex frequencies.

In section 1.6.1. the role of the proton potential in relation to the internal modes was discussed. It was indicated that two types of splitting might occur: (1) due to coupling with the N-H stretching mode and (2) due to the tunnelling of the proton through the potential barrier. It is the former that gives rise to the

identification of the split frequencies as characteristic of the donor and acceptor moieties. If splitting is due to tunnelling then it should be the same for all modes and this is evidently not the case. Clearly donor/acceptor splitting depends upon the degree of coupling that occurs between the N-H stretching mode and the internal mode.

If the further splitting observed in the fluorophosphate samples, which it is considered is due to crystallisation, were due to prototropism then firstly it should be observed for all internal modes and secondly it should be reduced considerably in the deuterated complex. In any case it is suggested that the freezing of the solutions into a glass creates permanently asymmetric proton potentials in which the tunnelling rate is effectively zero.

The evidence of the low temperature experiments is consistent with the pseudo-static asymmetric potential well. At room temperature it has not proved possible to identify two frequencies for any internal mode in the complex under consideration⁶⁹. Generally the one frequency observed for each mode at room temperature reappears in the low temperature assignment as a salt-like complex band. The similarity between the salt and complex spectra was noted by Clements and Wood⁶⁹. However close examination at room temperature has only been made upon the ν_{6a} feature. This mode was studied in solutions containing excess base and those with excess salt and only one component could be found. Now ν_{6a} appears to

be an exceptional mode since its complex frequency is far from that of either the free donor or acceptor; in addition the 628 cm^{-1} band observed is believed to be due to the acceptor moiety (see Chapter 5). It therefore seems possible that the fact that no complex band could be detected in the region of the free base band of ν_{6a} in excess salt solution cannot be extended to the other modes. An examination of other modes in excess salt solution might reveal second, base-like, complex bands, providing the separation between free salt and free base frequencies is sufficiently large.

CHAPTER 5.

5. THE INFRA-RED SPECTRA OF TWO ASYMMETRIC COMPLEXES

5.1 Introduction

The importance of identifying the provenance of the single frequencies observed for the internal modes in symmetric complexes was outlined in section 1.6.1. The low temperature work described in the previous chapter has gone some way towards resolving the problem, however there is a second line of attack which involves the study of asymmetric complexes between pyridine itself and other, stronger and weaker pyridine-type bases. Previously published work with such asymmetric complexes indicates that intercomparison can be made between complexes containing different bases using the parameter ΔpK_a (the difference in pK_a 's between the two bases).

Clearly it is to be expected that the proton potential function in asymmetric complexes should be asymmetric. Whether it contains a double or single minimum the proton will then be localised on the side of the stronger base. Therefore, in complexes between pyridine and a stronger base the internal modes of the pyridine ring should be characteristic of pyridine in a proton acceptor role, whilst association with a weaker base should lead to internal pyridine modes of the proton donor type. One advantage of using asymmetric complexes is that the internal modes of the two bases are generally non-coincident. Consequent confusion over the provenance of each band should be eliminated, however the use

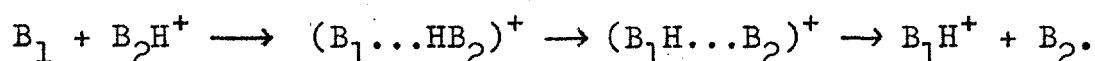
of mixed samples does increase the number of species and hence the number of bands observed.

Previously asymmetric complexes containing pyridine have generally been studied^{12,74} with bases stronger than pyridine. In this chapter two bases not previously employed and both weaker than pyridine, 3-bromopyridine and 2-chloropyridine (3-Brpy and 2-Clpy), have been used.

5.2 The Nature of the Species Observed

In previous examinations of asymmetric complexes the salt of the stronger base has been dissolved in the weaker base or in a suitable solvent in which the concentration of the weaker base has been high. Detailed examination⁷⁴ of the intensities of various peaks characteristic of the dissolved species has been used to determine the nature of the species observed and it has been concluded that the asymmetric complex is present in much higher concentrations than either of the symmetric complexes formed by the two bases.

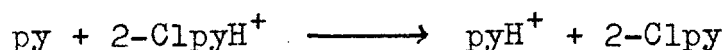
A simple consideration shows that this is so, despite the fact that, as shown in section 2.10, the equilibrium constant for the asymmetric complex is lower than that of either of the symmetric complexes. In solutions composed as described in the previous paragraph the presence of the two species B_1H^+ and B_2 (where $pK_a(B_1) < pK_a(B_2)$) can only be obtained by the formation of the asymmetric complex and dissociation to give the less stable products by proton transfer to the weaker base:



Only when this reaction has occurred can the symmetric complexes be formed. Since the proton potential function in the asymmetric complex favours the form $(B_1 \dots HB_2)^+$, the concentration of B_1H^+ and B_2 must be low and hence that of the symmetric complexes is extremely small. Naturally the solutions described contain equal total quantities of base B_2 and proton since both are introduced in the form of salt $B_2H^+X^-$. If extra protons are added, e.g. with $B_1H^+X^-$, then they can contribute to the formation of $(B_1HB_1)^+$, the B_2 base molecules remaining fully protonated.

In the present study solutions containing pyH^+ and 3-Brpy or 2-Clpy in the ratio 1M : 2 or 4M in acetonitrile have been used. The absence of bands characteristic of py , 3-Brpy H^+ or 2-Clpy H^+ has been taken to imply that it is the asymmetric complex that is observed in each case.

It is of note to report that whilst the making-up of solutions as described in the previous paragraph proceeded normally, when 2-chloropyridinium salt was dissolved in pyridine the sample became warm and a yellow discolouration occurred. It is suggested that this observation indicates that the overall reaction



is taking place.

5.3 The 3-Bromopyridine Systems

Before examining the spectra of the asymmetric complexes it is necessary to establish the characteristic frequencies of the base, salt and symmetric complex of 3-Brpy for comparative purposes. The infra-red spectra of the base^{70,75} and the salt, 3-BrpyHCl⁷⁵ have been published. Although the notation used is the same as that for pyridine, there is no necessity for the vibrations described to be the same since the normal coordinates for the vibrations in the two bases are different due to the different point groups to which they belong.

5.3.1 The (3-Brpy₂H)⁺ complex

The spectra of solutions in acetonitrile of free salt and of base and salt together are presented in figures 5.1 and 5.2 respectively. In figure 5.2 the peaks due to free base are indicated. Table 5.1 shows the assignment of the band frequencies to the internal modes. The paucity of bands which can be assigned to the complex is due to the weakness of the complex - both free base and salt must be assumed to be present since there are no clear instances of absent free component bands. Presumably many complex bands are concealed underneath the component bands. There is no doubt that complex is formed since the characteristically broad doublet of the ν_s , N-H stretching band, is observed at about 2500 and 2200 cm⁻¹.

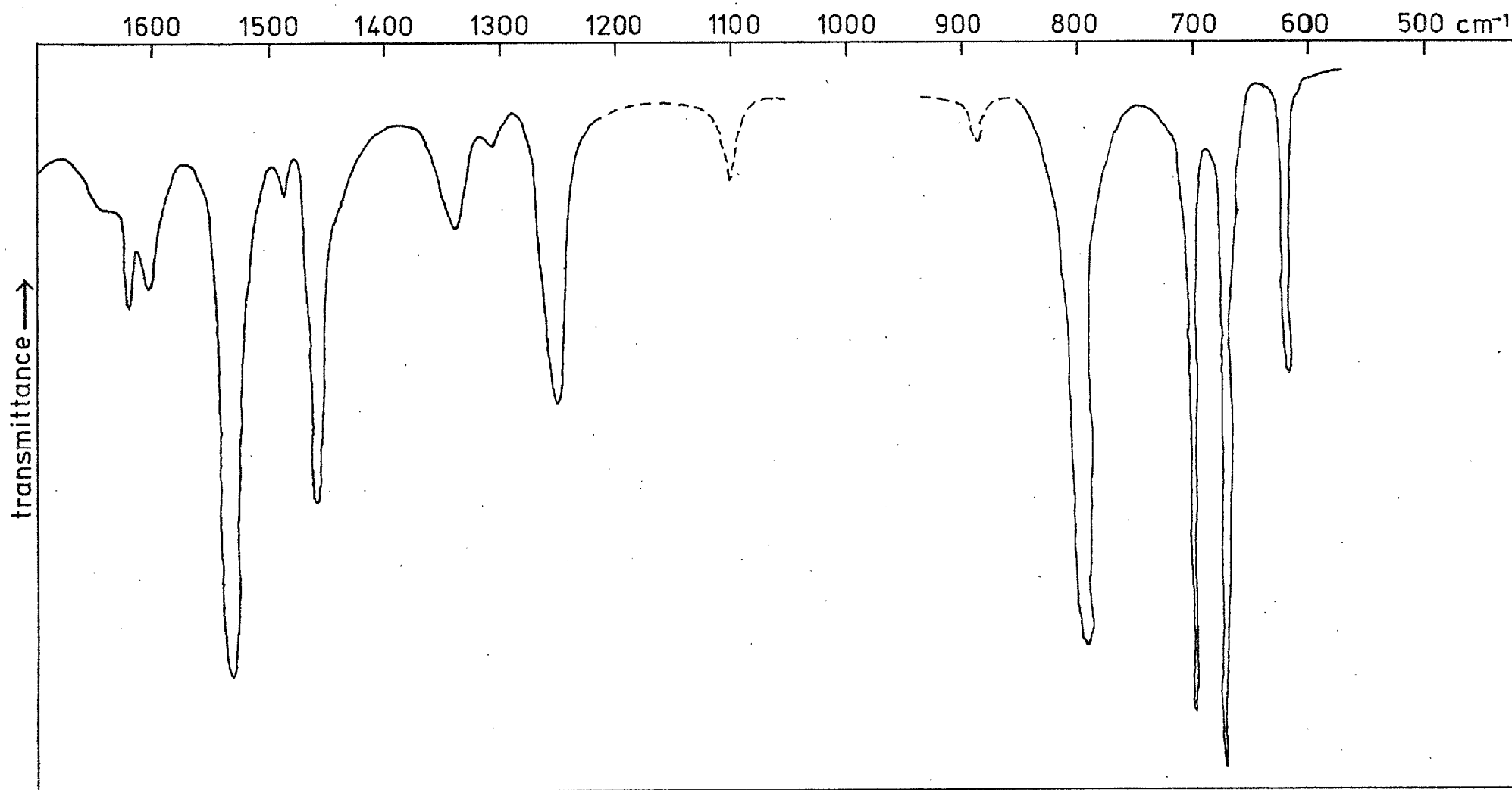


Figure 5.1. The infra-red spectrum of 3-BrpyH⁺, 1700-600 cm⁻¹.
All solvent and counter-ions bands excluded.

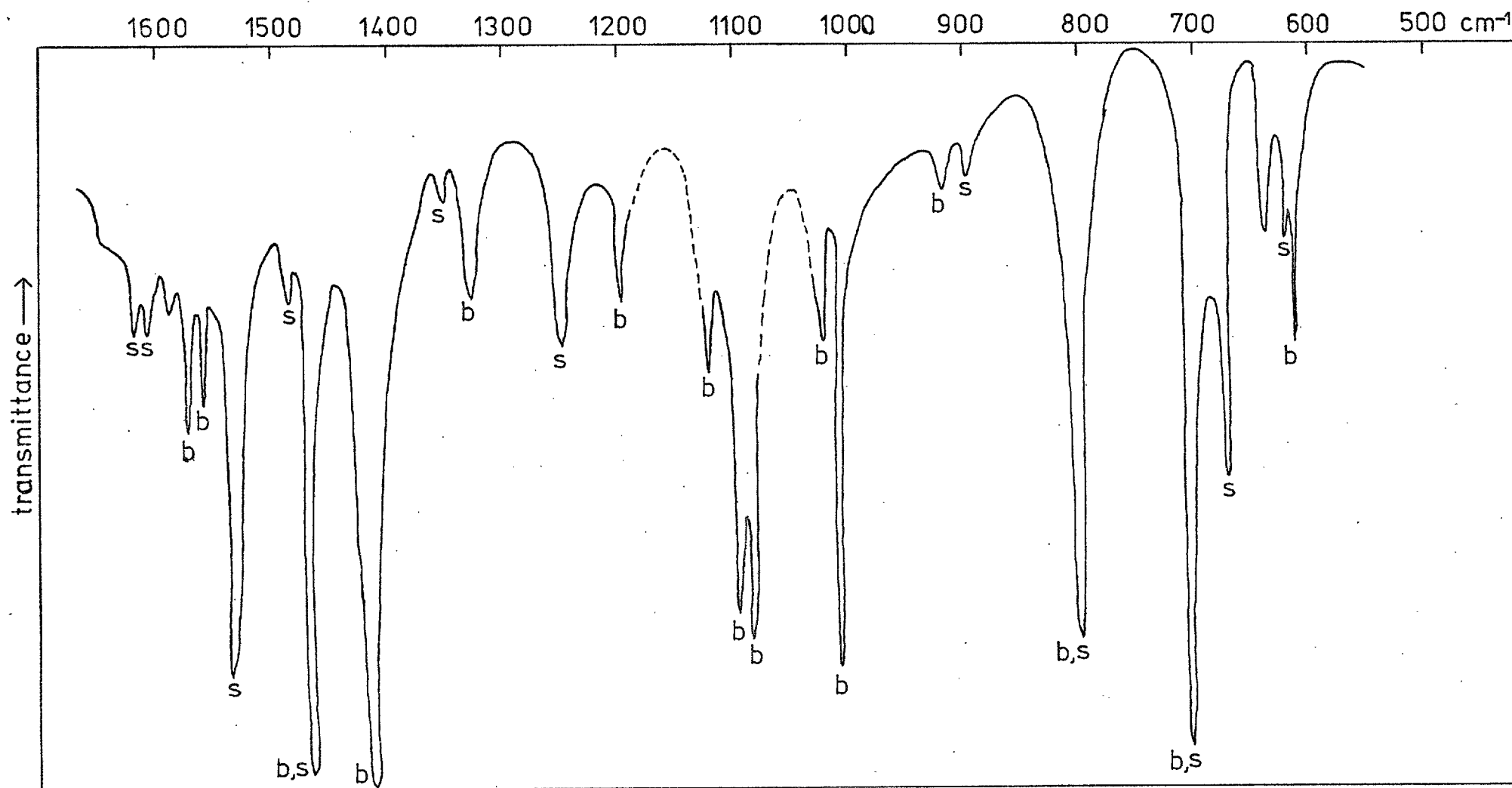


Figure 5.2. The infra-red spectrum of $(3\text{-Brpy}_2\text{H})^+$ in excess free base, $1700\text{-}600\text{ cm}^{-1}$. All counter-ion bands excluded. Bands due to free base marked b. Bands due to free salt marked s.

TABLE 5.1 Internal modes of $(3\text{-Brpy}_2\text{H})^+$
(frequencies in cm^{-1})

Assignment	3-Brpy	3-BrpyH ⁺	$(3\text{-Brpy})_2\text{H}^+$
ν_{8a}	1571 m	1608 m	(1587)
ν_{8b}	1557 m	1622 m	1587 w
ν_{19a}	1464 s	1534 s	(1466)
ν_{19b}	1414 s	1463 s	
		1487 w	
ν_{14}	1320 m	1339 m	
ν_b	-	1250 m	
ν_3	1220 w		
ν_{9a}	1188 m		
	1117 m		
ν_{18b}	1096 s	1102 w	
ν_{13}	1087 s		
ν_{18a}	1024 m		
ν_1	1007 s		
ν_{10a}	917 w	884 w	
ν_5	947 w		
ν_{10b}	789 s	793 s	
ν_{12}		701 s	
$\nu_4 (\nu_{11}?)$	702 s	670 s	668 sh
ν_{6b}	612 s	621 m	636 m

5.3.2 The Asymmetric Complexes (3-BrpyHpy)⁺

The complexes of 3-bromopyridine with four isotopically substituted pyridine salts (pyH⁺, pyD⁺, d₅pyH⁺ and d₅pyD⁺) have been studied. In all spectra a search has been made for free pyridine and 3-BrpyH⁺ bands. The absence of several of each indicates that the asymmetric complex predominates. For example, free pyridine bands at 1218, 1148, 1068 and 603 cm⁻¹ are definitely absent, whilst those of perdeuterated pyridine at 1301 and 962 cm⁻¹ do not appear in the relevant spectra. Secondly, whilst we cannot exclude the presence of (3-Brpy₂H)⁺ on these grounds because so few of its bands have been identified, we can be sure that free salt, 3-BrpyH⁺, is absent since two strong bands at 1534 and 670 cm⁻¹ are missing.

The relevant spectra are displayed in figures 5.3 and 5.4. The assignments shown in tables 5.2 and 5.3 exclude the characteristic frequencies of 3-bromopyridine which was always in excess. Differences in frequencies between the asymmetric complex and the relevant complex (py₂H)⁺ are in most cases small but finite, thus aiding assignment of the pyridine bands.

Of particular interest is the region 640-620 cm⁻¹. Here the ν_{6b} modes of the 3-Brpy system and the ν_{6a} modes of the pyridine system are found. In previous work^{66,69} the ν_{6a} mode of pyridine has proved to be of great value in the analysis of spectra because of its marked dependence upon the nature of the species and the fact that it appears in a region relatively free from obscuration by

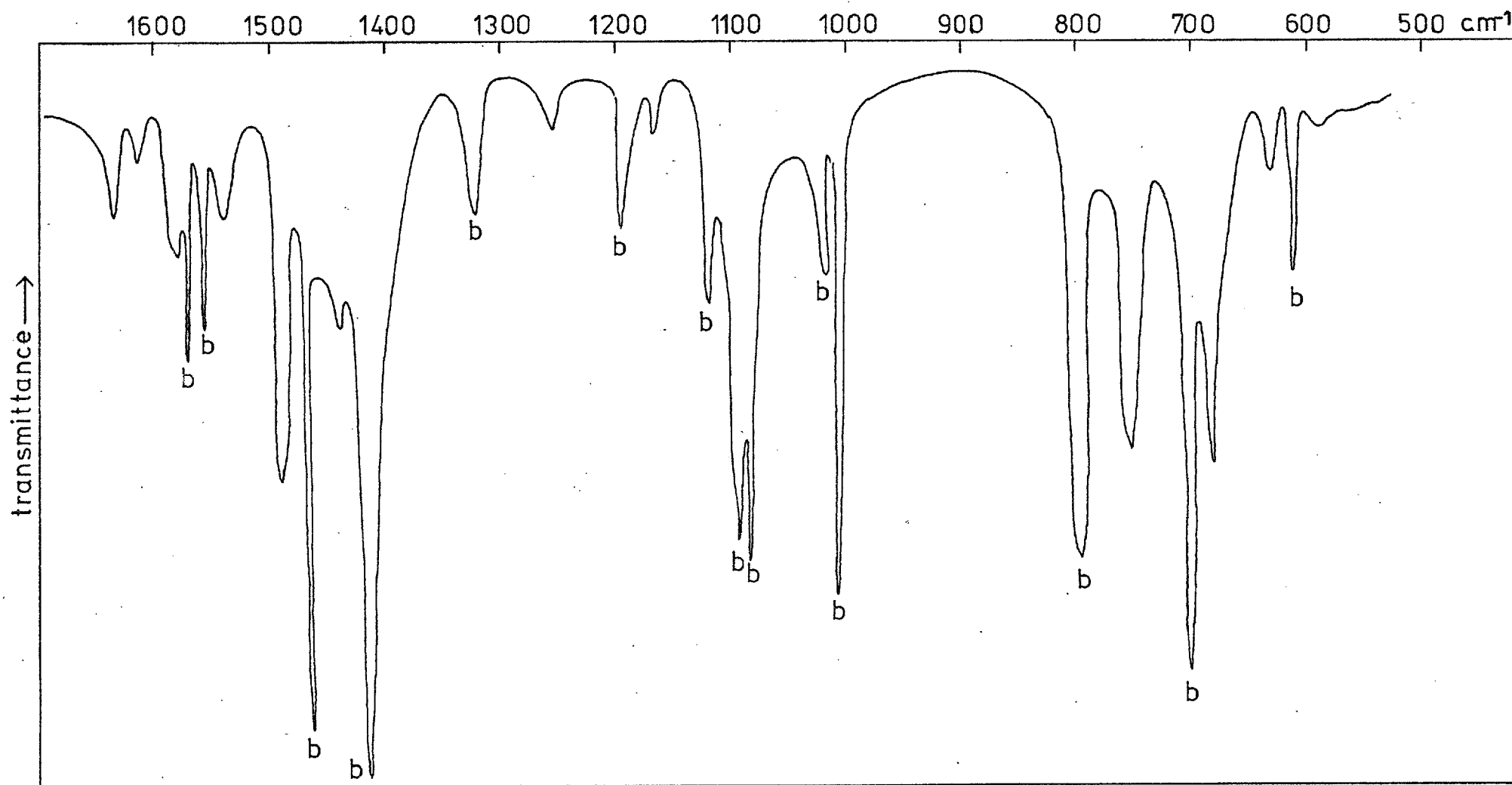


Figure 5.3. The infra-red spectrum of $(3\text{-BrpyHpy})^+$ in acetonitrile, $1700\text{-}500\text{ cm}^{-1}$, (3-Brpy in excess). All counter-ion bands excluded. Bands due to free 3-Brpy marked b.

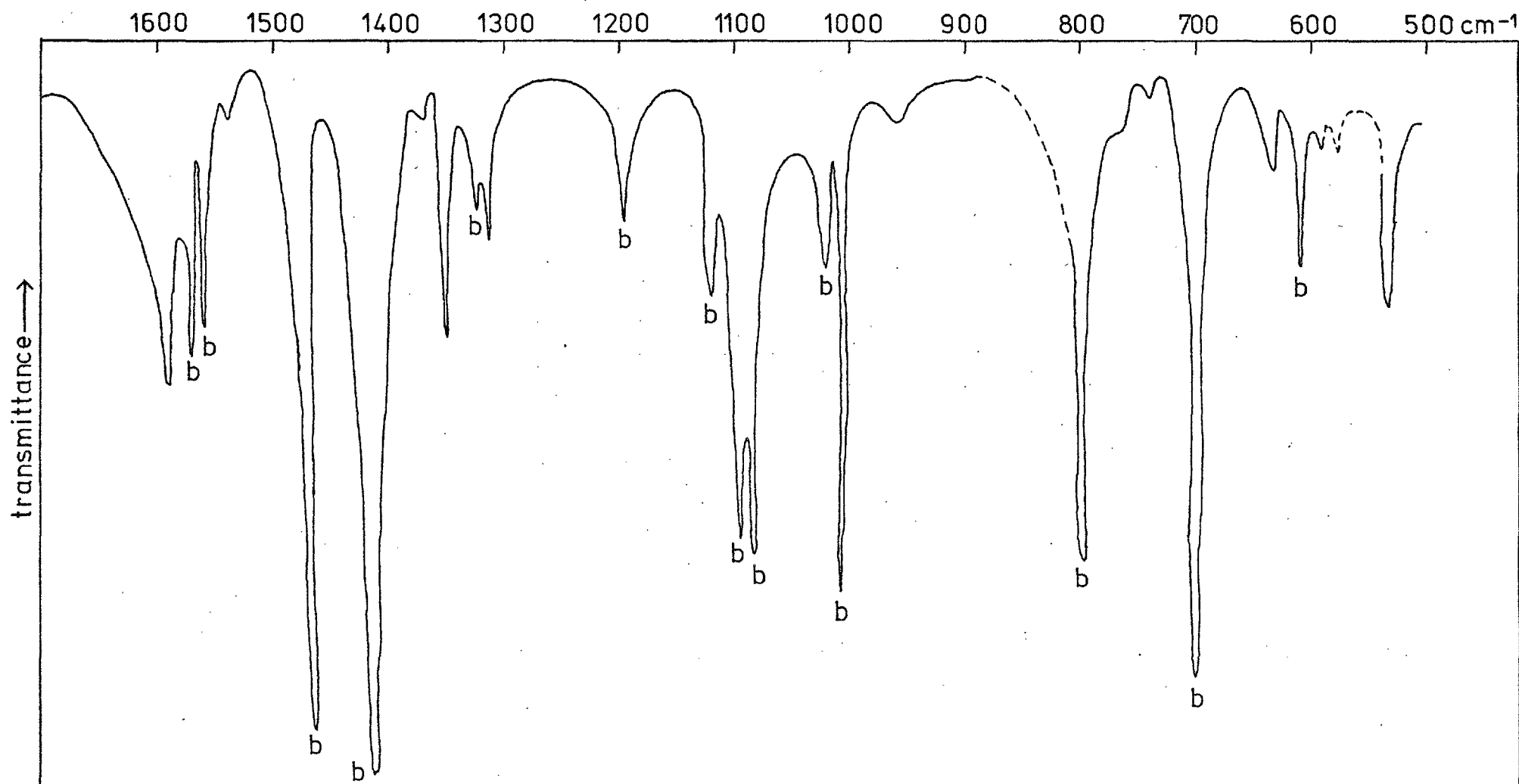


Figure 5.4. The infra-red spectrum of $(3\text{-BrpyHd}_5\text{-py})^+$ in acetonitrile, $1700\text{-}500\text{ cm}^{-1}$ (3-Brpy in excess). All counter-ion bands excluded. Bands due to free 3-Brpy marked b.

TABLE 5.2 INTERNAL MODES OF (3-BrpyHpy)⁺
 (Frequencies in cm⁻¹; the region 1150-1000 cm⁻¹ is obscured for the asymmetric complexes by counter-ion absorption.)

Assignment	py ₂ H ⁺	(3-BrpyHpy) ⁺	py ₂ D ⁺	(3-BrpyDpy) ⁺
ν_{8b}	1639 m	1637 m	1637 m	1634 m
ν_{8b}	1603 m	1613 m	1600 m	1583 m
ν_{19a}	1549 m	1540 m	1575 m	-
ν_{19b}	1493 s	1489 s	(1482)	1486 s
ν_{14}	-	-	-	(1301)?
ν_{9b}	1255 m	1250 m	-	1253 w
ν_{9a}	1205 s	1201 w	1206 s	1203 w
ν_3	-	-	-	-
ν_{15}	1167 m	-	1170 m	1165 w
ν_{18b}	1087 w	-	1079 w	-
ν_{18a}	1040 s	-	1037 s	-
ν_1	1007 s	-	1005 s	-
ν_{10b}	948 m	902 sh	-	-
ν_4	(762)sh	-	-	762 sh
ν_{11}	684 s	679 s	684 s	681 m
ν_{6b}	-	632 m	-	630 m
(3-Brpy)				
ν_{6a}	628 s	-	625 s	-

TABLE 5.3 Internal modes of (3-BrpyHd₅py)⁺
(frequencies in cm⁻¹)

Assignment	(d ₅ py ₂ H) ⁺	(3-BrpyHd ₅ py) ⁺	(d ₅ py ₂ D) ⁺	(3-BrpyDd ₅ py) ⁺
ν _{8a}	1592 m	1590	1590 m	1586
ν _{8b}	1562 sh	(1537)	1562 sh	-
ν _{19b}	1479 m	1468 sh	1375 m	1372
ν _{19a}	1348 s	1348	1340 s	1341
ν ₁₄	1309 s	1311	1292 s	1289
ν _b	-	-	934 m	-
ν ₁	975 m	962	975 m	(951)
ν ₅	778	776	-	-
ν _{10a}	(740)	(740)	-	-
ν _{6b} (3-Brpy)	-	631	-	630
ν _{17a}	(628)	-	630 sh	-
ν _{6a}	606 s	-	600 s	-
ν ₁₁	521 s	531	522 s	529

other bands. In all four asymmetric complexes a band appears at about 631 cm^{-1} . In symmetric $(\text{py}_2\text{H})^+$ and $(\text{py}_2\text{D})^+$ the ν_{6a} band is at 628 and 625 cm^{-1} respectively and in the $(3\text{-Brpy}_2\text{H})^+$ complex 636 cm^{-1} has been assigned to ν_{6b} . That the feature at 631 cm^{-1} appears in all four asymmetric complexes implies that it is due to the 3-bromopyridine moiety, which has the role of proton acceptor. What then has become of the ν_{6a} mode of pyridine? Either it is concealed under the 631 cm^{-1} band or it has disappeared. We can neither prove nor disprove the former suggestion for certain since no accurate intensity measurements have been made. However the similar size of the peaks in $(3\text{-BrpyHpy})^+$ and $(3\text{-BrpyHd}_5\text{py})^+$ does imply that no strong pyridine-type band is concealed beneath the former. If the ν_{6a} mode has truly disappeared from 628 cm^{-1} then it may be argued that this characteristic frequency is due to pyridine acting as the proton acceptor in the symmetric complex.

In no other internal mode is the evidence for assignment sufficiently good. Only at 1587 cm^{-1} has another $(3\text{-Brpy}_2\text{H})^+$ band been assigned. There is a complex band at approximately this frequency in all but $(3\text{-BrpyHpy})^+$. Assignment in this region is unsatisfactory since in going from the symmetric pyridine complex to the asymmetric complex the frequency of ν_{8b} rises for py but falls for d_5py .

It is worth noting that in general the difference in frequency between a mode in a symmetric pyridine complex and the corresponding asymmetric complex is small,

and that ν_{8b} appears to be the principal exception. The other frequencies obtained for the pyridine moiety in the asymmetric complex will be used in a later chapter.

5.4 The 2-Chloropyridine Systems

5.4.1 The $(2\text{-Clpy}_2\text{H})^+$ complex.

The symmetric complex has been satisfactorily observed, and a number of new bands have been assigned to the internal modes. Figure 5.5 shows the spectrum of the free base and salt in acetonitrile and that of the mixed solution is shown in figure 5.6. Again the work of Green et al.⁷⁰ has been used as a basis for the assignments given in table 5.4.

Although a large number of new bands have been identified in the spectrum of the mixed solution and they have been allocated to the symmetric complex, assignment to particular modes has proved most difficult. In many instances this is due to the apparent change of strength in the band (which may not necessarily be a bar to assignment) or to an extreme frequency shift upon complex formation.

It is clearly not possible to exclude the presence of free salt from the mixed solution, however the substantial reduction in relative intensity of some bands characteristic of free salt suggests that in some cases complex and free salt bands are coincident. For example the free salt band at 621 cm^{-1} is considerably weakened (its complex counterpart is at 633 cm^{-1}) whereas that at

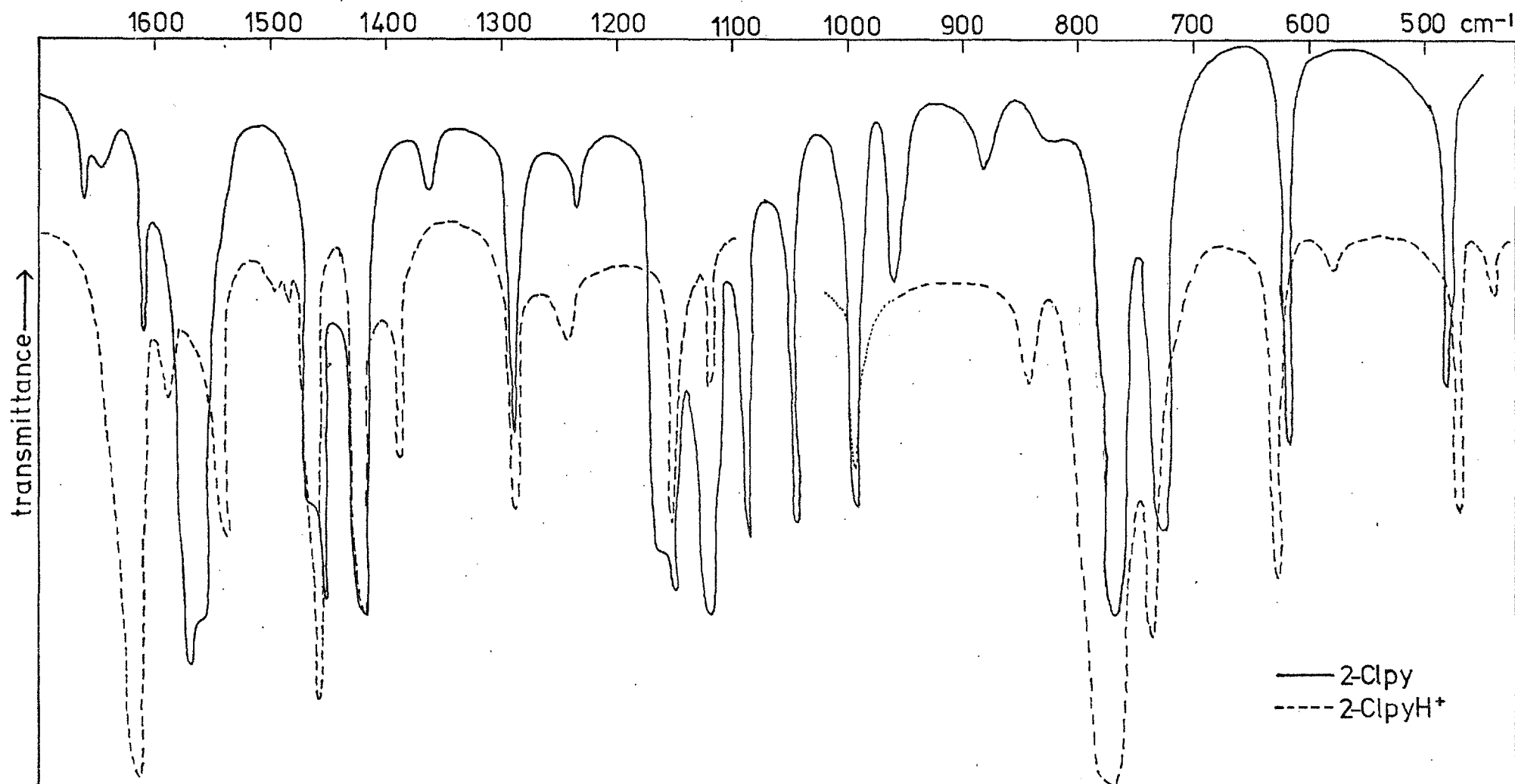


Figure 5.5. The infra-red spectra of 2-Clpy and 2-ClpyH⁺ in acetonitrile, 1700-400 cm⁻¹. All counter-ion and solvent bands excluded.

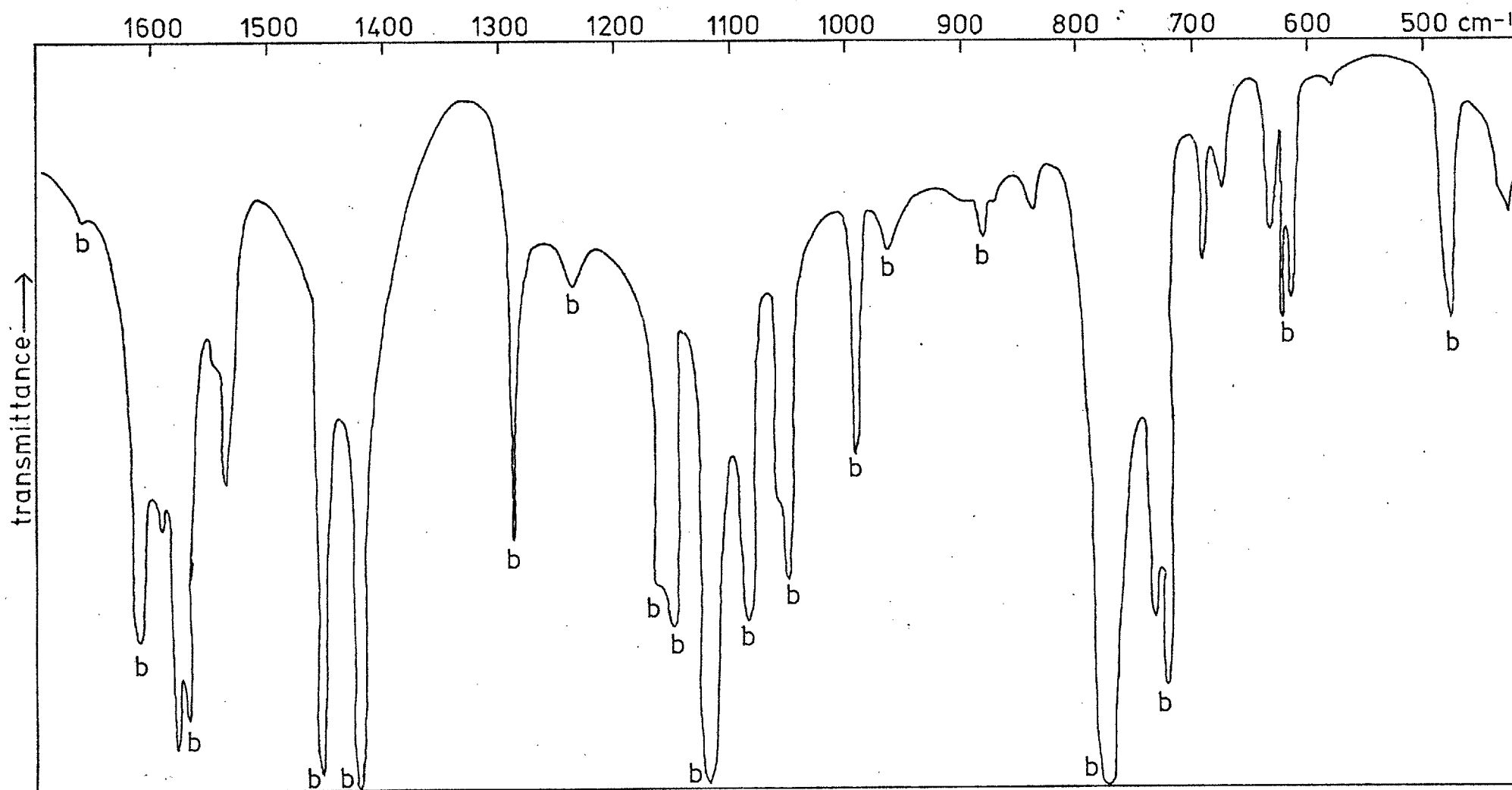


Figure 5.6. The infra-red spectrum of $(2\text{-Clpy}_2\text{H})^+$ in excess free base, $1700\text{-}400\text{ cm}^{-1}$. All counter-ion bands excluded. Bands due to free 2-Clpy marked **b**.

TABLE 5.4 The 2-Clpy system (frequencies in cm^{-1})

Assignment	2-Clpy	2-ClpyH ⁺	(2-Clpy ₂ H) ⁺
ν_{8a}	1575 s	1618 vs	1617
ν_{8b}	1568 sh	1581 w	1593
	-	1537 m	(1544)
ν_{19a}	1454 s	1461 s	-
ν_{19b}	1421 s	1422 s	-
ν_{14}	1361 w	1388 m	-
ν_3	1288 m	1287 m	-
$\nu_{9b?}$		1240 w	-
ν_{9a}	1150 m	1150 m	1161
ν_{13}	1119 s	1120 w	-
ν_{18b}	1085 s	990 m	-
ν_{18a}	1045 s	obscured by solvent	-
ν_1	990 m		1006
			962?
ν_{10a}	880 m	842 w	(894)
			871
ν_{10b}	771 vs	771 vs	-
ν_{12}	725 s	734 m	(690)
			673
ν_{6b}	617 m	621 m	633
ν_{11}	481 m	479 m	-
ν_{6a}	424 m	439 m	439
ν_{16a}	404 m	-	-

1618 cm^{-1} appears stronger in the mixed solution than in the free salt solution and this is ascribed to the presence of an underlying complex band. It is certain that complex is formed since the characteristic ν_s doublet is observed.

5.4.2. The Asymmetric Complexes (2-ClpyHpy)⁺

Studies of asymmetric complexes between 2-chloropyridine and pyH^+ , pyD^+ and d_5pyH^+ were attempted. These complexes proved extremely unstable to dissociation under a variety of conditions and it was not possible to obtain any firm assignments of peaks due to the complex.

First, solutions of pyridinium salt and excess 2-chloropyridine in acetonitrile were considered. As a test of complex formation the ν_s (N-H stretching) band region ($2800\text{--}2000\text{ cm}^{-1}$) was observed. Although a weak band centred at about 2570 cm^{-1} was seen, no band corresponding to the low frequency portion of the doublet could be detected. It was therefore decided to use the base, 2-Clpy, as solvent. Any differences between the solution spectrum and the free base spectrum would then be due to the pyridinium ion or to complex formation.

The first observation of importance is the low solubility of pyridinium salts in 2-Clpy. Although saturated solutions were used, the counter-ion absorption was unusually small. Again the structure of the ν_s band was weak with only the high frequency section of any significant size. In the ring mode region the proof of the absence of free pyridinium salt was made difficult

both by the small size of the new features and by the fact that some of the largest free pyridinium bands, if present, would be concealed by strong 2-chloropyridine absorption. In none of the three cases was there a clear cut example of an absent free salt band.

It is notable that 2-chloropyridinium salt dissolves quite satisfactorily in 2-chloropyridine to give the symmetric complex (ν_s doublet at 2520 and 2000 cm^{-1}). Observations in the ring mode region indicate again that the presence of free salt may not be eliminated. Complex bands appear as observed in acetonitrile solution and as described in the previous section.

Initially it appears possible that the unsatisfactory nature of these observations might be due to the large value of ΔpK_a involved ($pK_a(\text{py}) = 5.17$, $pK_a(2\text{-Clpy}) = 0.72$ therefore $\Delta pK_a = 4.45$)^{59,76}. In section 2.10 it was proposed that if ΔpK_a were to become too large the hydrogen-bonded complex might be unstable to dissociation giving the free components. However Clements and Wood⁷⁴ have studied a large range of asymmetric complexes and have detected one such between 2-fluoropyridine and 2,4,6-trimethylpyridine ($\Delta pK_a = 7.92$).

Alternatively steric hindrance to hydrogen-bond formation may be the factor responsible, however this would not explain the satisfactory observation of the symmetric complex $(2\text{-Clpy}_2\text{H})^+$ which would be expected to be even more sterically hindered.

CHAPTER 6

6. BAND-WIDTH MEASUREMENTS IN THE INTERNAL MODE REGION OF SYMMETRIC COMPLEXES

6.1 Introduction

One of the reasons proposed for a failure to observe band splitting in the internal modes of symmetric pyridine complexes at room temperature is that the splitting is too small to be resolved. Even studies⁶⁶ with narrow slit widths designed to improve resolution down to 0.1 cm^{-1} have failed to reveal splitting or abnormal band shapes which might be interpreted as the sum of two or more independent bands.

In this chapter the results of measuring the band-width (the width of the absorbance band measured at its half-height) of the ν_{6a} (ring elongation) mode are considered. Two effects are of particular interest. Firstly if the single band observed is the sum of two separate bands due to the proton donor and acceptor roles of the pyridine ring then a substantially broader band should be expected for the complex compared to that of each free constituent. Secondly if the broadening is due to proton tunnelling then there should be a significant narrowing of the band upon deuteration at the bridging atom. The two effects correspond to two different spectral situations as indicated in figure 6.1. In the latter case the broadening in internal modes due to tunnelling should be constant for all modes affected. For proton donor and acceptor bands which are nearly

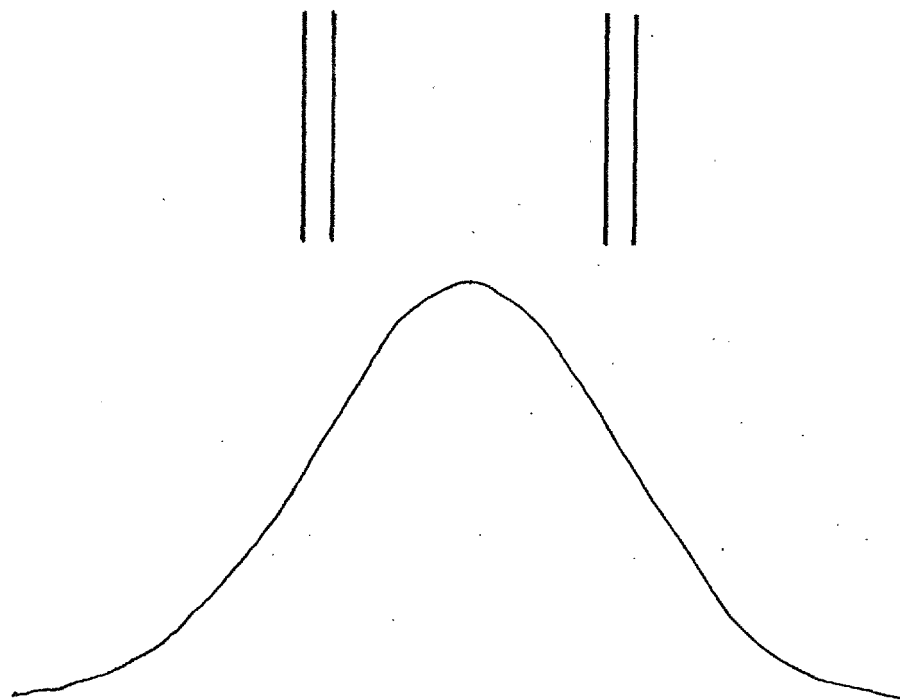


Figure 6.1a : Splitting due to the tunnelling mode is very small and the proton donor and acceptor bands are almost coincident giving a single broadened band.

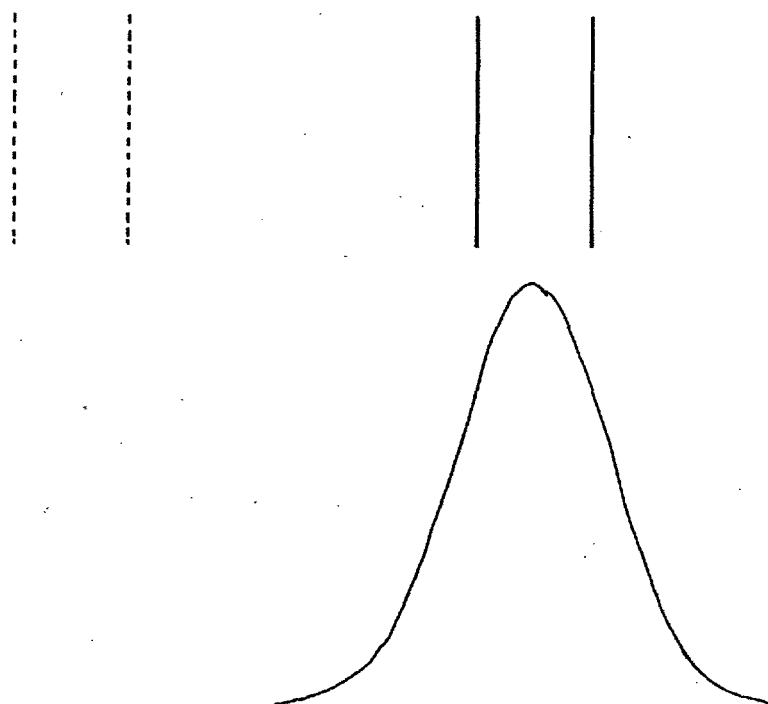


Figure 6.1b : The observed band is due only to one half of the complex cation. Splitting due to tunnelling is small and results in band broadening.

coincident the broadening should vary, as each mode is affected to a different extent.

Kreevoy and Mead⁷⁷ have demonstrated the use of Raman band-widths in measuring proton transfer rates in the range 10^{-11} - 10^{-14} s. They applied the method to the 1433 cm^{-1} symmetric C=O stretching band in trifluoroacetic acid/trifluoroacetate mixtures in aqueous solution. The band-width in the mixture was observed to be 7.2 cm^{-1} wider than its value of 15.0 cm^{-1} in the spectrum of free trifluoroacetate with excess sodium hydroxide.

6.2 Measurements and Results

As in previous work^{66,69} the ν_{6a} band has provided the most reliable data of any of the internal modes. This is because in the pyridine systems considered, there are generally large frequency differences between the free acceptor, donor and complex bands (the frequencies of the bands measured in this work are presented in table 6.1). Additionally the region is free of other internal mode bands so that a clear view of the ν_{6a} bands may be taken. No other band has proved susceptible to satisfactory measurements because of overlapping with other bands.

TABLE 6.1 The frequencies of the ν_{6a} bands in the systems considered (in cm^{-1}).

	Free Acceptor	Free donor	Complex
pyridine	603	{ 610 (H) 603 (D)	628 (H-bridge) 624 (D-bridge)
d ₅ -pyridine	580	587	603
4-methylpyridine	515	(521)*	535

* 4-mepyHCl complex.

In all cases measurement has been made upon spectra drawn on the absorbance scale. These were obtained by conversion from the transmittance spectra produced by the spectrometer, taking into account the use of the attenuation and scale-expansion facilities. No intercomparison of absorbances may be made because of the varying spectrometer conditions employed, however the band-widths are invariant to such linear variations in absorbance. The half-height was measured from a linear base-line drawn across the bottom of the band. No attempt was made to use a curved base-line or one derived from the spectrum of the neat solvent.

It should be noted that satisfactory band-width data cannot be obtained from transmittance spectra since the results produced are not comparable unless they have been corrected for the magnitude of the band. Transmittance spectra exaggerate small peak heights and underestimate those of large peaks compared to absorbance, which is a scale linear in concentration and sample thickness. Thus the position at which the band-width is measured is dependent upon the nature of the scale chosen. It is not suggested that the procedures used here are the most accurate. Yarwood⁷⁸ has presented a comprehensive discussion of the techniques required for very accurate measurement. The results presented here do however provide evidence of some real effects observed.

The results presented in this chapter fall into three categories, depending upon the experimental conditions:-

(A) Solutions of proton donor in excess proton acceptor - three symmetric complexes (pyridine, d_5 -pyridine and 4-methylpyridine) were considered and the spectra are presented in figures 6.2 - 6.4.

(B) Solutions in acetonitrile of the pyridine system (figure 6.5) and

(C) the pyridine system in acetonitrile at two different temperatures (figure 6.6). At the lower temperature (-30°C) the sample is still liquid.

The measured band-widths are presented in table 6.2. The estimated error in the measurement of band-widths in A and B is $\pm 0.5 \text{ cm}^{-1}$ and in C $\pm 1.0 \text{ cm}^{-1}$. The shoulder which appears in some spectra at 621 cm^{-1} is due to the fluoroborate anion.

It is first evident that the complex bands are wider than either the free salt or free base bands. Secondly there is a distinct sharpening of the complex band upon deuteration of the bridging atom. Thirdly there is a narrowing of the bands upon cooling the sample. There is a notable sharpening of the free pyridine and d_5 -pyridine bands when complex is present and in acetonitrile solution. There is a possible sharpening of the free proton donor band when base is added to the solution.

The integrated intensities of the bands can be seen to increase substantially upon complex formation. Compare the spectra for the two protonated samples in figure 6.5. In the excess pyridine sample the concentrations of free base, free salt and complex are approximately 1.4, 0.1 and 0.7 M respectively, whilst in excess

TABLE 6.2. Band-width measurements
(in cm^{-1}) upon the ν_{6a} mode.

	<u>Free</u> <u>Acceptor</u>	<u>Free</u> <u>Donor</u>	<u>Complex</u>
<u>A. Solutions of proton donor in excess proton acceptor.</u>			
neat py	7.4	-	-
pyH ⁺ /py	5.1	-	9.2
pyD ⁺ /py	5.3	-	8.6
neat d ₅ py	5.8	-	-
d ₅ pyH ⁺ /d ₅ py	4.2	-	8.6
neat 4-mepy	4.3	-	-
4-mepyH ⁺ /4-mepy	4.1	-	8.8
<u>B. Solutions in acetonitrile.</u>			
[py] ₀	[pyH ⁺] ₀		
2.1	1.7	3.4	2.9
1.2	1.5	-	3.0
2.1	0.8	4.1	-
0	1.0	-	3.5
2.7	0.8(pyD ⁺)	4.1	-
<u>C. The temperature effect.</u>			
[py] ₀ = [pyH ⁺] ₀	{ +30°C -30°C	-	-
= 0.5M in CH ₃ CN			
[py] ₀ = [pyD ⁺] ₀	{ +30°C -30°C	-	-
= 0.5M in CD ₃ CN			

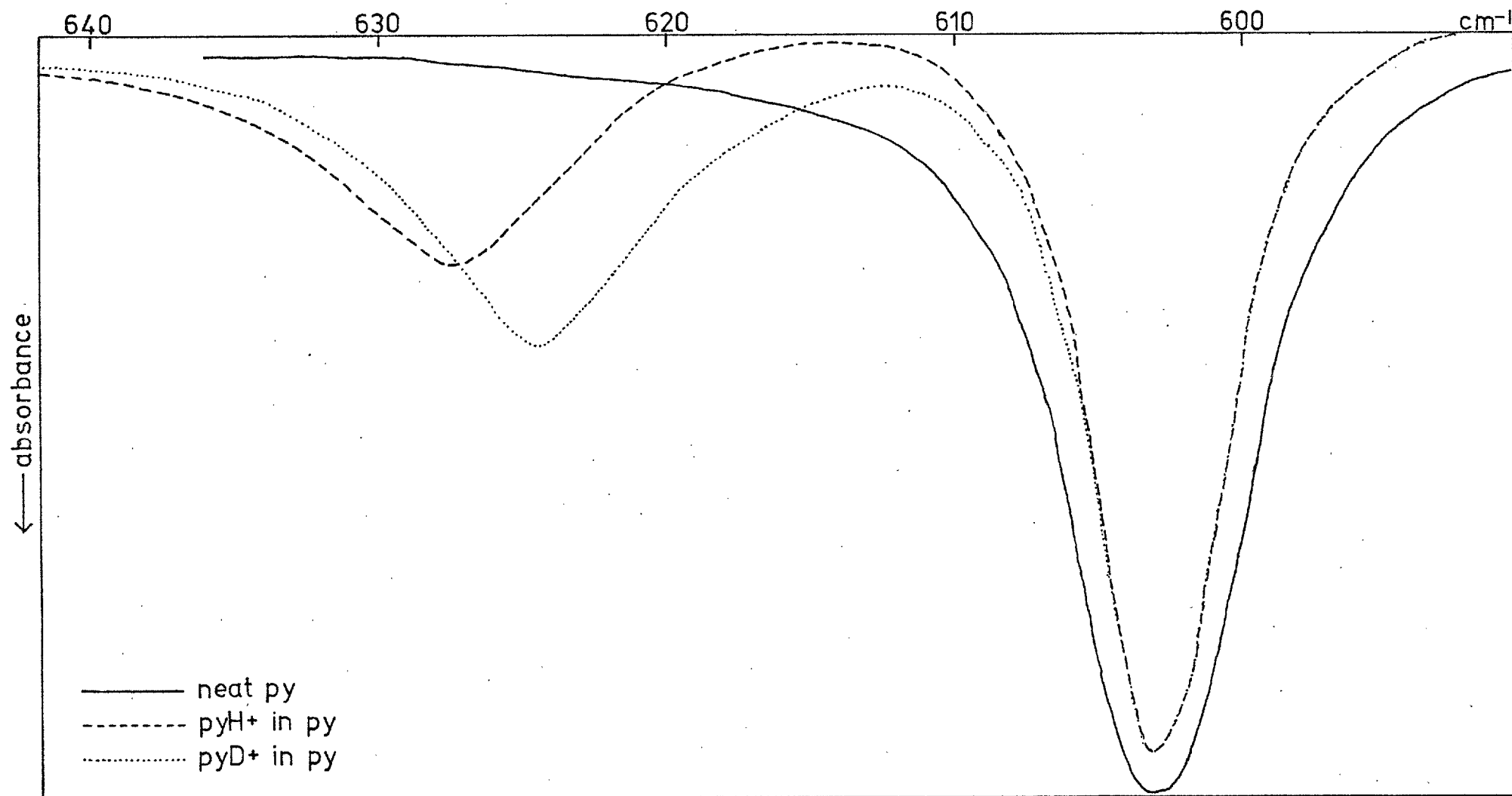


Figure 6.2. The infra-red spectra of py and of $(\text{py}_2\text{H})^+$ and $(\text{py}_2\text{D})^+$ in free base, 640-590 cm^{-1} . The three spectra are not on the same absorbance scale.

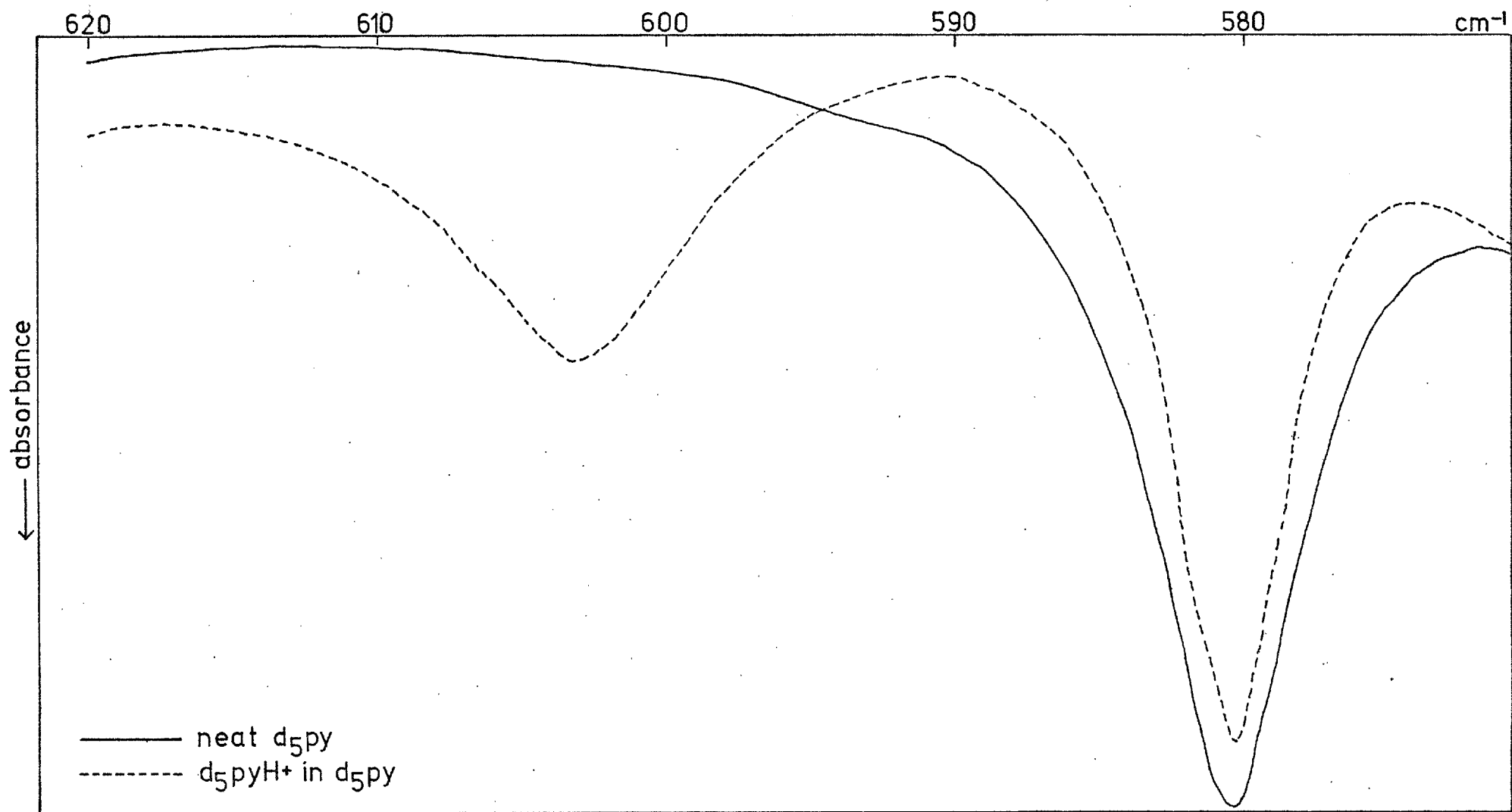


Figure 6.3. The infra-red spectra of $d_5\text{py}$ and of $(d_5\text{py}_2\text{H})^+$ in free base, 620-570 cm^{-1} . The two spectra are not on the same absorbance scale.

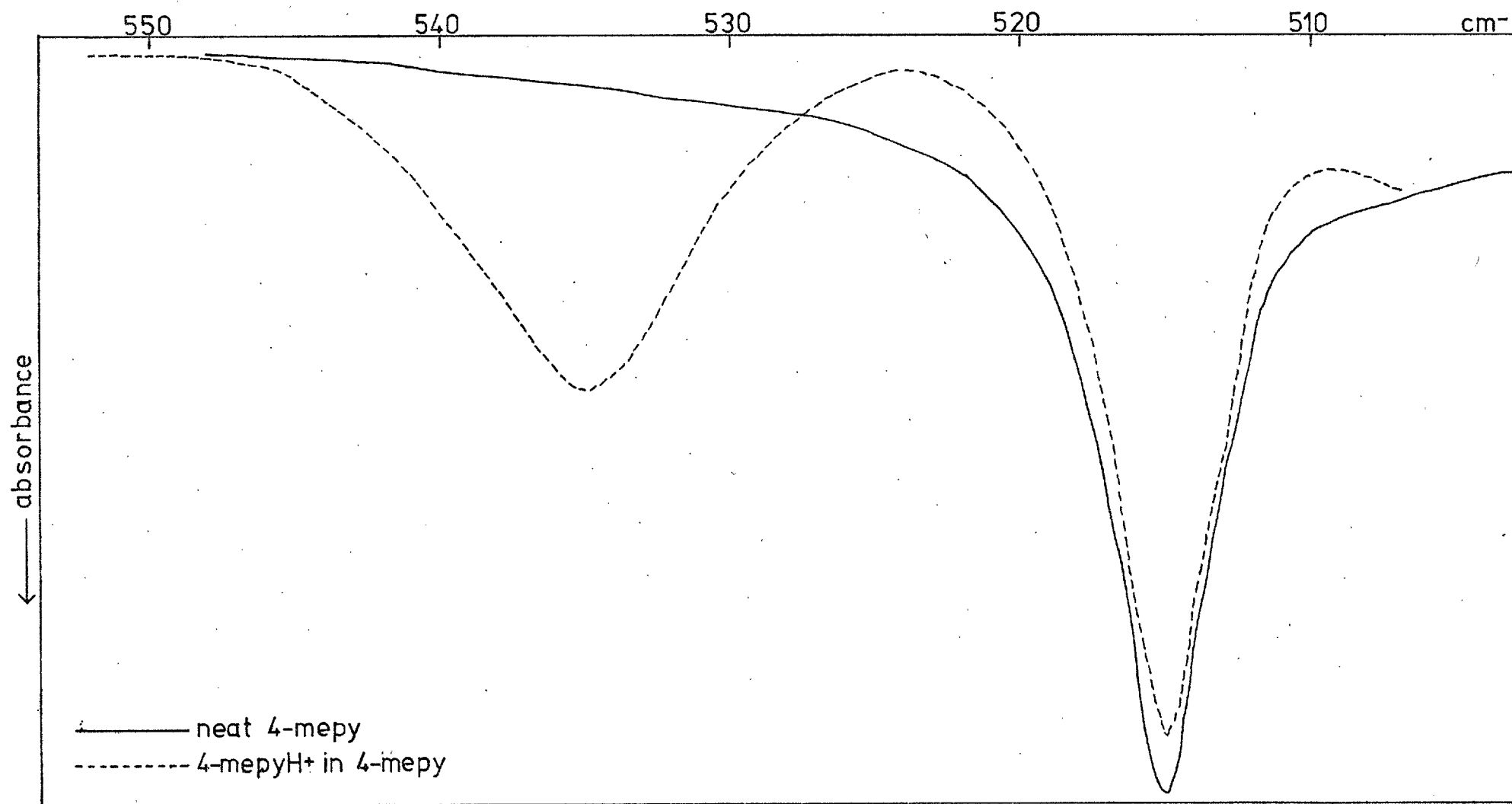


Figure 6.4. The infra-red spectra of 4-mepy and of $(4\text{-mepy}_2\text{H})^+$ in free base, 550-500 cm⁻¹. The two spectra are not on the same absorbance scale.

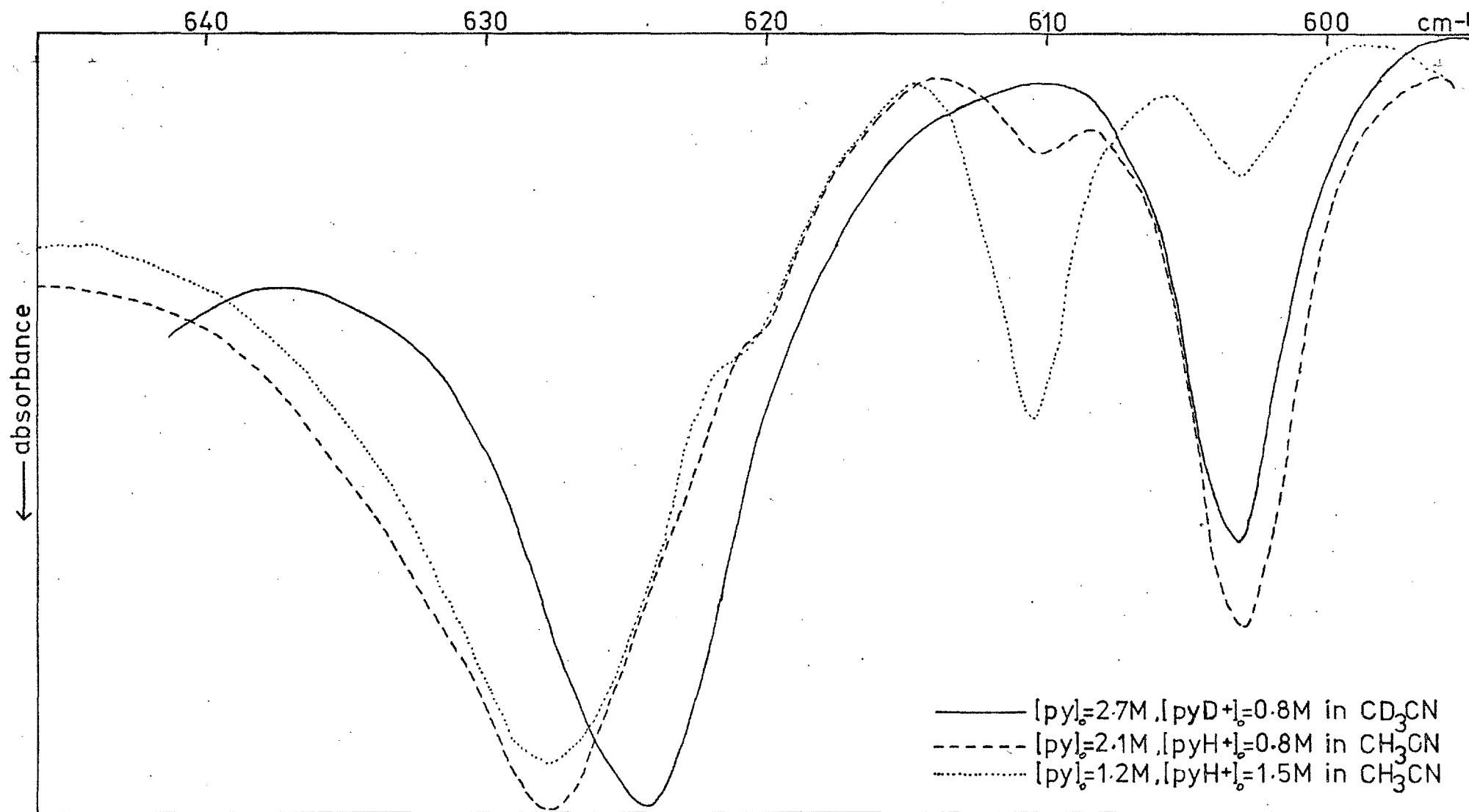


Figure 6.5. The infra-red spectra of three solutions in acetonitrile of the pyridine system, 640-600 cm^{-1} . The three spectra are not on the same absorbance scale.

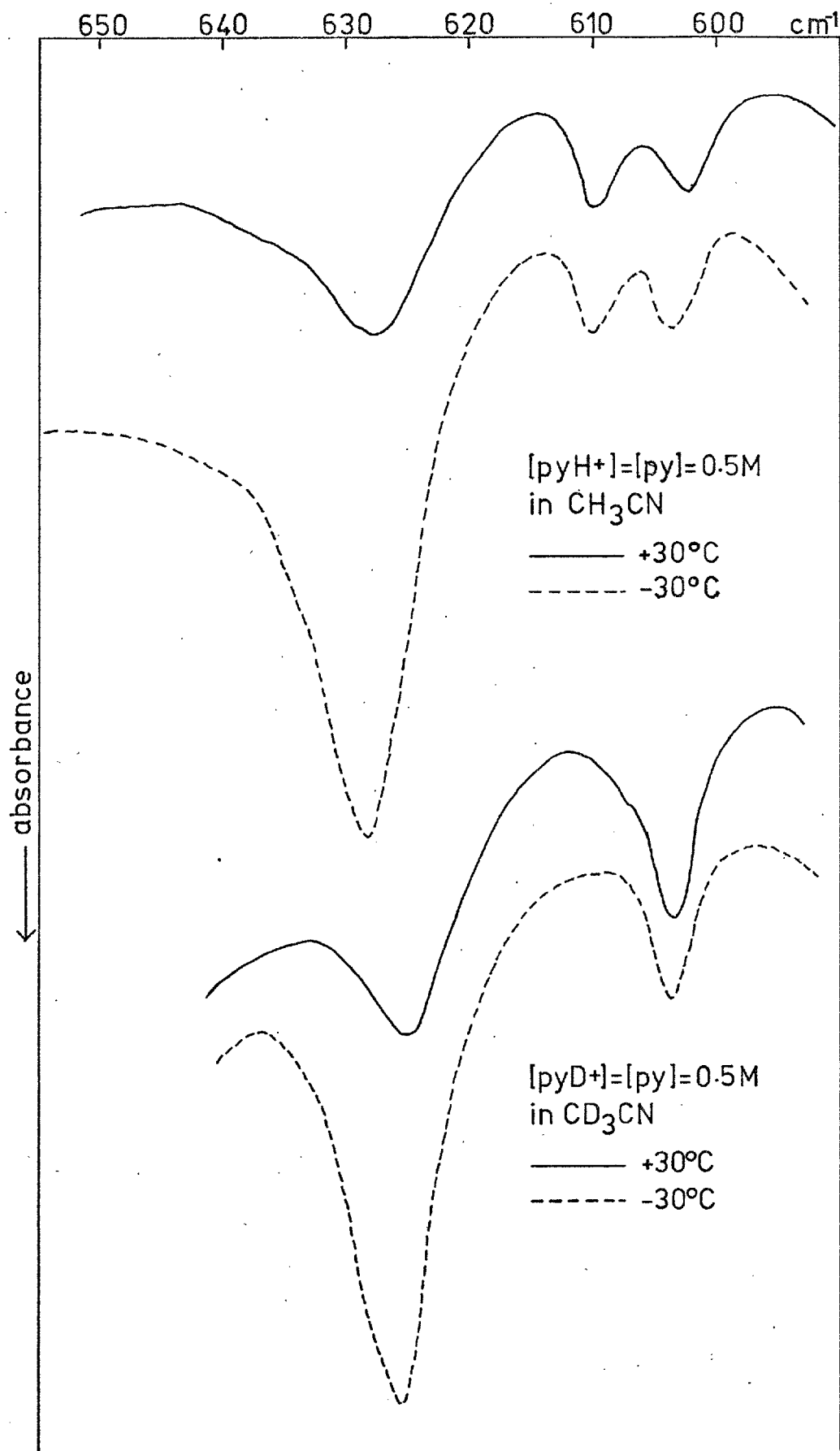


Figure 6.6. The infra-red spectra, at $\pm 30^\circ\text{C}$, of py and pyH⁺ or pyD⁺ in acetonitrile. The spectra are not on the same absorbance scale.

pyridinium the figures are 0.4, 0.7 and 0.8 M. It can be seen that, in the former case, even with a two-fold excess of free base over complex, the area under the complex band is some three times larger than that under the base band. Where the complex and free salt concentrations are approximately equal the band of the former is almost nine times more intense than that of the latter.

6.3 Discussion

There are a number of factors upon which the width of a vibrational band depends without consideration of the hydrogen-bonding effects discussed in section 6.1. Yarwood⁷⁹ has considered the changes in intensity and band-width of the internal modes of pyridine when a charge-transfer complex, py-ICl, is formed in benzene. The ν_{6a} band shifts to 629 cm^{-1} and the band-width falls from 6.0 to 5.0 cm^{-1} ; however there is a six-fold increase in the integrated intensity of the band. On the other hand Yarwood⁷⁸ also reports that considerable band broadening occurs when the complex, py-SO₂, is formed.

The two generally important determinants of band-width are the rotational sub-structure and the life-time of the excited state. The former depends upon the rotational diffusion of the molecule in the solution and hence upon the bulk of the molecule. Complexing gives a bulkier molecule and hence the rotational substructure becomes finer and the vibrational band narrows. The life-time of the excited state depends upon the relaxation pathways available for dissipating the absorbed energy.

If there is good coupling between modes then vibrational relaxation is fast and the uncertainty of the excited state energy level is high giving rise to a broad band. Additional vibrational relaxation may occur through interaction with the fluctuating local electric field. Consequently variations in band-width upon complexation are not necessarily due to the effects of the hydrogen-bond.

The general conclusion of chapter 4, that the single bands observed at room temperature for each ring mode are those of the proton donor moiety, suggests that the effect being sought in this band-width study is not the splitting into donor and acceptor bands, although only one frequency could be identified for the ν_{6a} mode. It is therefore likely that the band broadening upon complexing may be attributed to those influences described by Yarwood. In addition the loose nature ("floppiness") of the complex in the bending, stretching and torsion of the hydrogen bond which may pertain in solution would be expected to broaden all the bands in the spectrum of the complex relative to those of the uncomplexed components.

The narrowing of the ν_{6a} complex band upon deuteration of the bridging atom is particularly pronounced in acetonitrile solution. At first sight it is easy to attribute this narrowing to a reduction in the tunnelling rate upon deuteration. In this case the natural band width might be, say, 7 cm^{-1} and the effect of tunnelling on the band in acetonitrile solution would then be 1.3 cm^{-1} for the deuteron and 4 cm^{-1} for the proton. The change from excess pyridine as solvent to

acetonitrile is significant for the proton but less so for the deuteron. This may be a sign of the environmental dependence of tunnelling discussed earlier.

The small degree of sharpening observed upon cooling the samples is quite likely to be attributable to the increased viscosity of the solution which prevents the rotation of the complex in the solution. If proton tunnelling is occurring from the ground state then its rate should be insensitive to temperature.

It is unfortunate that further measurements are not possible on the other internal modes because of overlapping of bands. In particular it would be of interest to know over what range the intensity enhancement of the internal mode bands occurs. Boobyer and Orville-Thomas⁸⁰ have proposed a pulsed charge cloud model to account for the rich enhancement of the $\nu_s(\text{O-H})$ stretching band in hydrogen bonded carboxylic acid dimers. In this model it is supposed that the O-H group induces a dipole in the highly polarisable lone pair electrons on the carbonyl oxygen atom. As O-H stretching occurs the induced dipole is altered giving a large overall dipole change in this vibration and an enhanced absorption. The strong ν_s band in symmetric pyridine complexes may arise from the same origin. If so, it might be expected that those vibrations of the ring which involve motion of the nitrogen would also undergo such enhancement. Clements⁶⁶ has drawn attention to the fact that even in saturated solutions of pyridinium salt in excess pyridine where the free pyridine must be over seven times more concentrated than

the complex, the bands assigned to complex are comparable in intensity with those of the base. Amongst the strongest bands are ν_{19a} , ν_1 and ν_{6a} (figure 6.7), all of which involve in-plane motion of the nitrogen. Boobyer and Orville-Thomas⁸⁰ point out that the frequency of the C=O vibration in the proton acceptor is little affected by hydrogen bonding, consequently in the $(py_2H)^+$ complex only those bands characteristic of the proton donor would be enhanced. The bands observed in room temperature samples of the symmetric pyridine complex are generally those of the proton donor (chapter 4) and this would be expected if the pulsed charge cloud model operated.

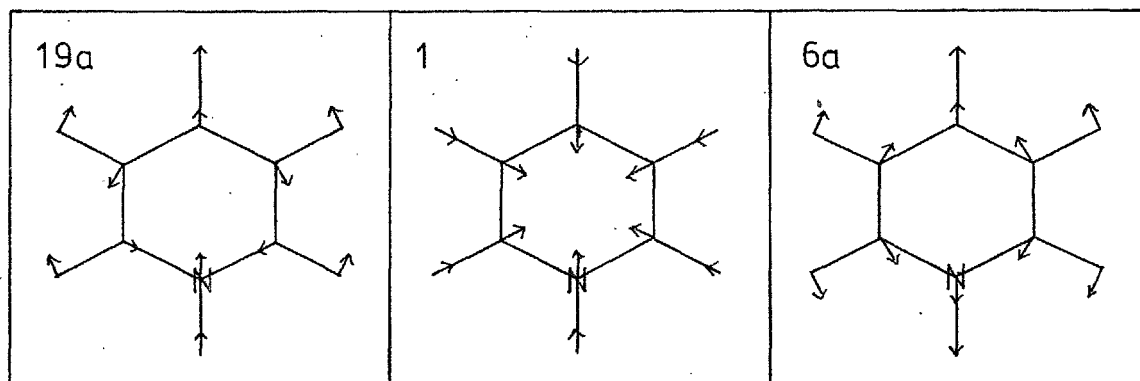


Figure 6.7. Normal co-ordinate displacements for pyridine⁸¹.

6.4 Conclusions.

It is evident that little information can be derived from the differences in band-widths between the complex and its uncomplexed components until the general causes of such variations have been elucidated. The deuteration effect is significant since it would be

expected only for reasons connected with hydrogen bonding. It would be valuable to make a careful search for any other internal mode whose band-width could be measured accurately, particularly if donor and acceptor bands could be identified beforehand. The ν_{6a} mode appears unique in several ways and may not provide a satisfactory example for study.

CHAPTER 7.

7. RANDOM FLUCTUATIONS IN THE N-N DISTANCE AS A CAUSE OF BAND BROADENING AND ENHANCED TUNNELLING RATES.

7.1 Introduction

Yarwood and Robertson⁸² have performed a detailed treatment of the interaction of the symmetric and antisymmetric hydrogen bond stretching frequencies. They have indicated that the best treatment requires that the ν_σ (A-B stretching) mode is strongly coupled to the random motion of the environment of the hydrogen bonded complex. The method explains the broadening of the ν_s (A-H stretching) band and enables the value of the ν_σ frequency to be calculated from an accurate fitting of the model to the experimental ν_s band-shape.

Dean and Wood¹² have additionally proposed that random fluctuations in the A-B distance due to environmental coupling would cause a variation in the barrier dimensions in a double minimum proton potential and hence proton transfer could occur at a rate faster than that implied by a static model. Borah and Wood²¹ have suggested a similar cause for the broadening of the ν_s band.

In this chapter the consequences of such random fluctuations are explored. The numerical results obtained are intended only to give a guide to the effect of such fluctuations. The fairly arbitrary choice of starting parameters and the number of assumptions made to simplify the model make quantitative calculations impossible at

this stage. However the several interesting conclusions drawn from the investigation make such an initial exploration of value. It should be noted that this model involves a symmetric double minimum potential and does not cover fluctuations in the electric field¹⁷ which lead to assymetrization of the potential function.

The work of Singh and Wood⁸ in which interaction between ν_s and ν_σ for the isolated symmetric hydrogen bond was treated provides a useful comparison. Although not described explicitly, the dependence of the tunnelling frequency, ν_τ (in their notation $|m,n\rangle_+ \rightarrow |m,n\rangle_-$), upon the state of the ν_σ vibration (variation in n) was shown in their figure 1. Because of the increase in the number of nodes in the ν_σ dimension in the probability function with increasing n , ν_τ falls as the effective region of tunnelling is reduced (figure 7.1). The increase in m decreases the effective barrier width and hence ν_τ rises; in this case the increasing number of nodes in the ν_s dimension only reduces the proton probability in the central region where tunnelling takes place. This does not reduce ν_τ which is a rate constant.

7.2 The nature of the fluctuation

Although an harmonic oscillator model has been used to derive the limits of the fluctuation it is not suggested that the fluctuation undergoes simple harmonic motion. The interaction sought in this chapter is not that between the N-N stretching vibration, ν_σ , and the N-H mode, ν_s ; that has been treated by Singh and Wood⁸.

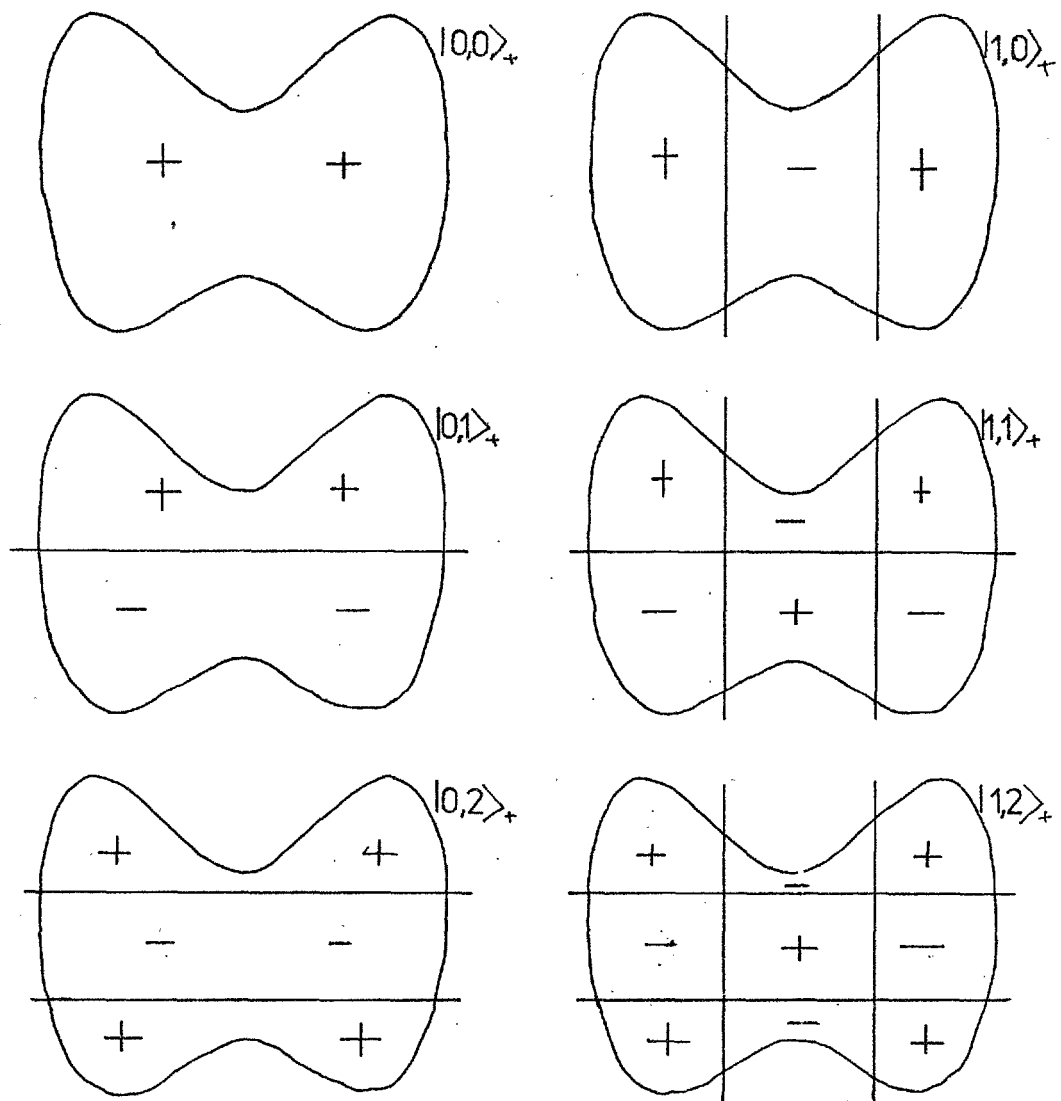


Figure 7.1 : Even wave-functions, $|m,n\rangle_+$, showing the increase in the number of nodes reducing the tunnelling region with increasing n (ν_0 states).

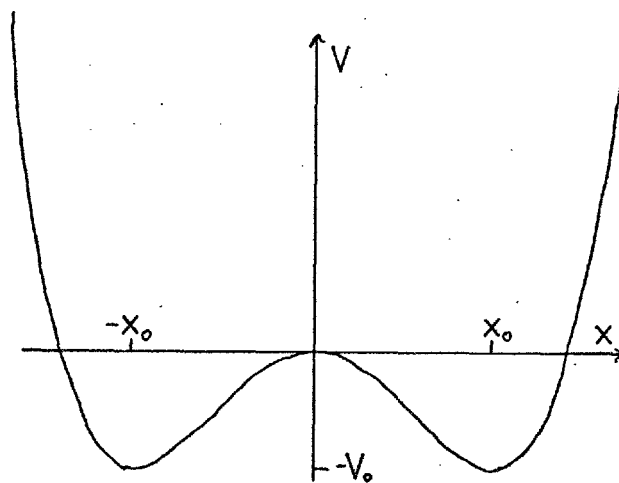


Figure 7.2 : A double-minimum potential function showing the essential parameters, x_0 and $-V_0$.

Interest presently lies in the random fluctuations of N-N caused by collisions in the solution. It has only been possible to treat the linear case here; however it may be seen that the bending of the hydrogen bond could also be studied. Indeed in a complete treatment the bending motion would have to be treated since the complex is floppy.

The model to be considered is therefore based upon the gaussian distribution of N-N distances and hence of x_0 . The gaussian distribution bears a strong resemblance to the ground state wave-function for the harmonic oscillator.

7.3 Calculation of the N-N fluctuation

It is initially assumed that the N-N distance undergoes harmonic oscillations. The extent of the fluctuation in the N-N distance may then be calculated from the force constant, K_σ , for the $(py_2H)^+$ complex which is⁶⁹ $0.319 \text{ mdyn } \text{\AA}^{-1}$. If the energy in this vibration is taken to be $\frac{1}{2}k_B T$ then

$$r^2 = \frac{k_B T}{K_\sigma}, \quad 7.1$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-16} \text{ erg K}^{-1}$) and $T = 300\text{K}$. The amplitude of the vibration, $2r$, is then $0.23 \text{\AA}$. From the crystal structure of the symmetric benzimidazole complex²¹, the N-N distance is found to be $2.79 \text{\AA}$ and the separation of the potential wells is estimated to be $0.70 \text{\AA}$. These are used as the equilibrium values in the following calculations, in which the well separation, $2x_0$, fluctuates between 0.6 and $0.8 \text{\AA}$.

7.4 The double minimum potential

A simple quadratic-quartic potential well is used:

$$2V = ax^2 + bx^4. \quad 7.2$$

The parameters are shown in figure 7.2. a is negative and b is positive. The introduction of a cubic term, which gives the asymmetric potential function, has not been treated.

From equation 7.2 it can be simply shown that

$$x_0 = (-a/2b)^{\frac{1}{2}} \quad 7.3$$

and

$$V_0 = -\frac{b}{2} x_0^4. \quad 7.4$$

The choice of a and b for the mean potential well was made on the basis of the ν_s (N-H stretching) frequency, 2530 cm^{-1} , in the symmetric, $(\text{py}_2\text{H})^+$, complex⁶⁹. (This is the transition $(N=0) \rightarrow (N=3)$ in figure 7.4b.). Then the parameters are:

$$a = -2.15 \text{ mdyn } \text{\AA}^{-1}$$

$$b = 9.86 \text{ mdyn } \text{\AA}^{-3}.$$

Figure 7.3 shows the two limiting potential curves for $x_0 = 0.30$ and $0.40 \text{ \AA}$. The value of b controls the shape of the potential at high values of x . In order to alter the barrier therefore a was varied. The two curves in figure 7.3 converge as x is increased but so slowly as to have no effect upon this model. Almost the entire variation in N-N separation is taken up between the two potential minima.

Equation 7.3 was used to evaluate a in order to vary the well-separation, $2x_0$.

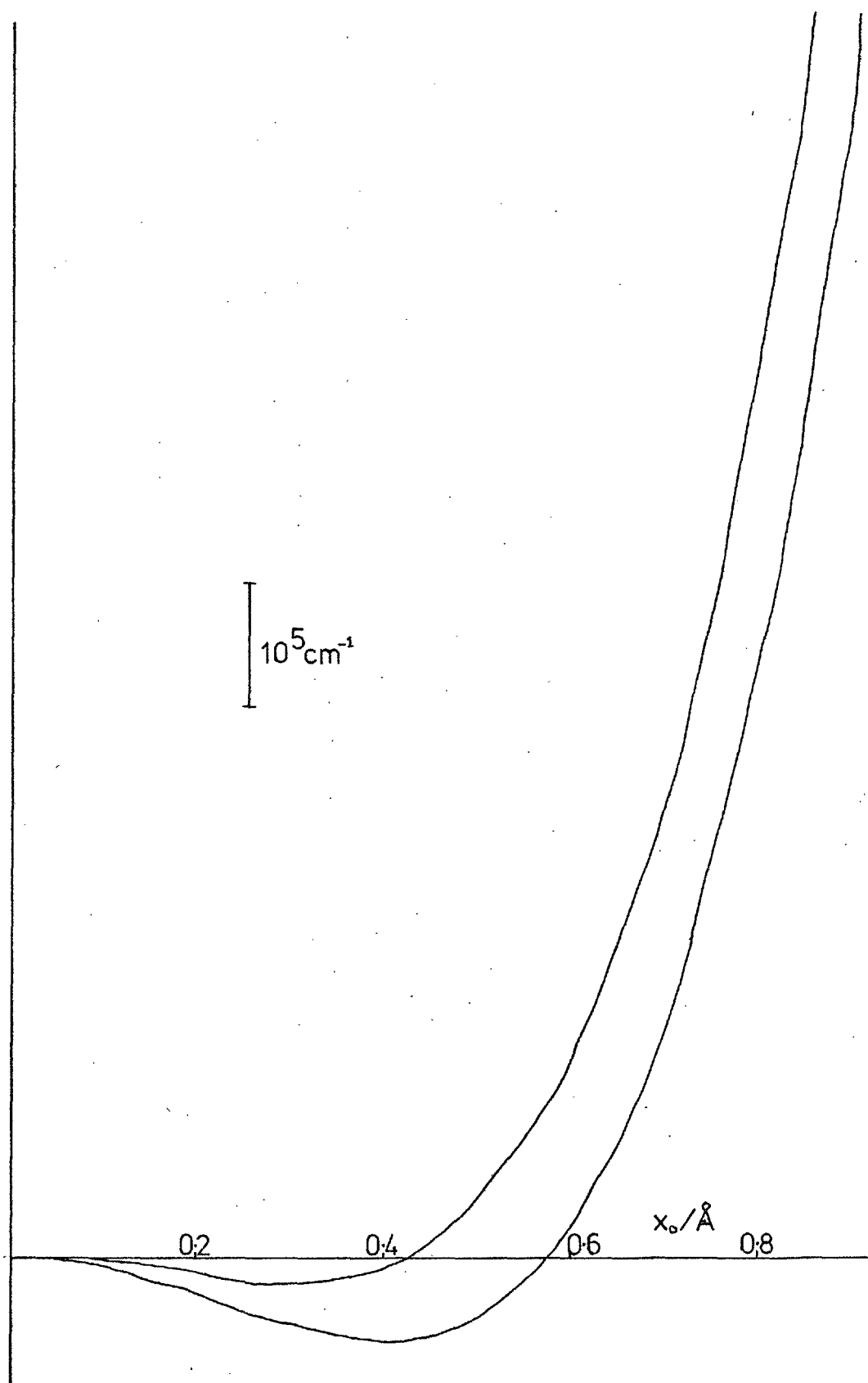


Figure 7.3. The two limiting potential functions. Only the right half of each is shown; the functions are even.

7.5 Calculation of the Energy Eigenvalues

For eleven values of x_0 , between 0.30 and 0.40 Å, the energy eigenvalues were calculated using the computer program DBMIN2⁹. Using twenty-one harmonic oscillator functions as a basis for expansion, this program solves the one-dimensional wave equation for the quartic-quadratic potential. Results for the proton and deuteron are represented in tables 7.1 and 7.2. Convergence has been confirmed for this program by Tayyari⁹. The precision of the eigenvalues was found to be better than 10^{-2} cm^{-1} . Some eigenvalues are shown superimposed upon the potential functions in figures 7.4 and 7.5. The variation in the eigenvalues for the proton is shown in figure 7.6, in which they are measured with respect to the well bottom.

7.6 The Tunnelling Transition, ν_T .

The effect of fluctuations in the N-N distance upon the tunnelling transition, ν_T , is illustrated in figure 7.7 for both protons and deuterons. If the N-N fluctuation is treated as a gaussian process then the probability of each individual barrier height and tunnelling frequency may be calculated for a given variance in the fluctuation process. Figure 7.8 illustrates the rate of tunnelling against x_0 for a variance, σ^2 , in x_0 of $4.0 \times 10^{-4} \text{ Å}^2$. A narrower distribution of the N-N fluctuation naturally sharpens this peak and the value of x_0 at which the tunnelling rate is a maximum is increased.

TABLE 7.1. Parameters, Eigenvalues and Transitions for a fluctuating barrier - proton results.

$x_o(\text{\AA})$	0.30	0.31	0.32	0.33	0.34	0.35	0.36	0.37	0.38	0.39	0.40
$(\text{mdyn}^{-a} \text{\AA}^{-1})$	1.77	1.89	2.02	2.15	2.28	2.42	2.56	2.70	2.85	3.00	3.16
$(\text{mdyn}^b \text{\AA}^{-3})$	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86
$V_o(\text{cm}^{-1})$	2010	2292	2602	2943	3316	3724	4168	4651	5175	5741	6353
N = 0	- 955	-1169	-1427	-1713	-2026	-2392	-2787	-3211	-3695	-4210	-4793
N = 1	- 826	-1075	-1363	-1670	-1998	-2375	-2777	-3205	-3692	-4208	-4792
N = 2	583	424	253	80	- 100	- 309	- 541	- 804	-1128	-1499	-1943
N = 3	1577	1326	1048	763	469	140	- 202	- 561	- 966	-1396	-1884
N = 4	2988	2712	2412	2113	1818	1507	1206	919	627	348	55
N = 5	4558	4246	3903	3557	3208	2829	2447	2061	1643	1219	758
N = 6	6294	5949	5573	5193	4810	4395	3977	3558	3110	2665	2197
N = 7	8167	7794	7385	6972	6556	6105	5649	5191	4696	4199	3667
$v_T(\text{cm}^{-1})$	129.8	94.0	64.2	42.6	27.5	16.7	9.90	5.73	3.11	1.65	0.81
$v_s(\text{cm}^{-1})$ {	2533	2495	2475	2475	2494	2532	2585	2650	2729	2814	2909
	1408	1498	1615	1750	1898	2066	2236	2400	2564	2710	2849

TABLE 7.2. Parameters, Eigenvalues and Transitions for a fluctuating barrier - deuteron results.

$x_0(\text{\AA})$	0.30	0.31	0.32	0.33	0.34	0.35	0.36	0.37	0.38	0.39	0.40
$\frac{-a}{(\text{mdyn } \text{\AA}^{-1})}$	1.77	1.89	2.02	2.15	2.28	2.42	2.56	2.70	2.85	3.00	3.16
$\frac{b}{(\text{mdyn } \text{\AA}^{-1})}$	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86	9.86
$V_0(\text{cm}^{-1})$	2010	2292	2602	2943	3316	3724	4168	4651	5175	5741	6353
$N = 0$	-1198	-1441	-1728	-2040	-2375	-2762	-3176	-3615	-4115	-4645	-5243
$N = 1$	-1178	-1429	-1722	-2037	-2374	-2761	-3175	-3615	-4115	-4645	-5243
$N = 2$	19	- 157	- 324	- 518	- 744	-1026	-1348	-1706	-2127	-2584	-3109
$N = 3$	367	146	- 104	- 368	- 648	- 972	-1318	-1691	-2120	-2581	-3108
$N = 4$	1216	1003	780	568	368	163	- 43	- 262	- 531	- 848	-1246
$N = 5$	2106	1848	1567	1283	995	679	357	23	- 350	- 744	-1193
$N = 6$	3123	2841	2534	2225	1917	1588	1266	958	648	364	- 77
$N = 7$	4231	3925	3590	3251	2911	2542	2172	1801	1402	1002	570
$\nu_T(\text{cm}^{-1})$	20.6	12.1	6.61	3.48	1.78	0.84	0.38	0.17	-	-	-
$\nu_s(\text{cm}^{-1}) \left\{ \right.$	1565	1587	1625	1672	1727	1791	1857	1924	1995	2064	2135
	1159	1272	1397	1518	1630	1735	1828	1909	1988	2061	2134

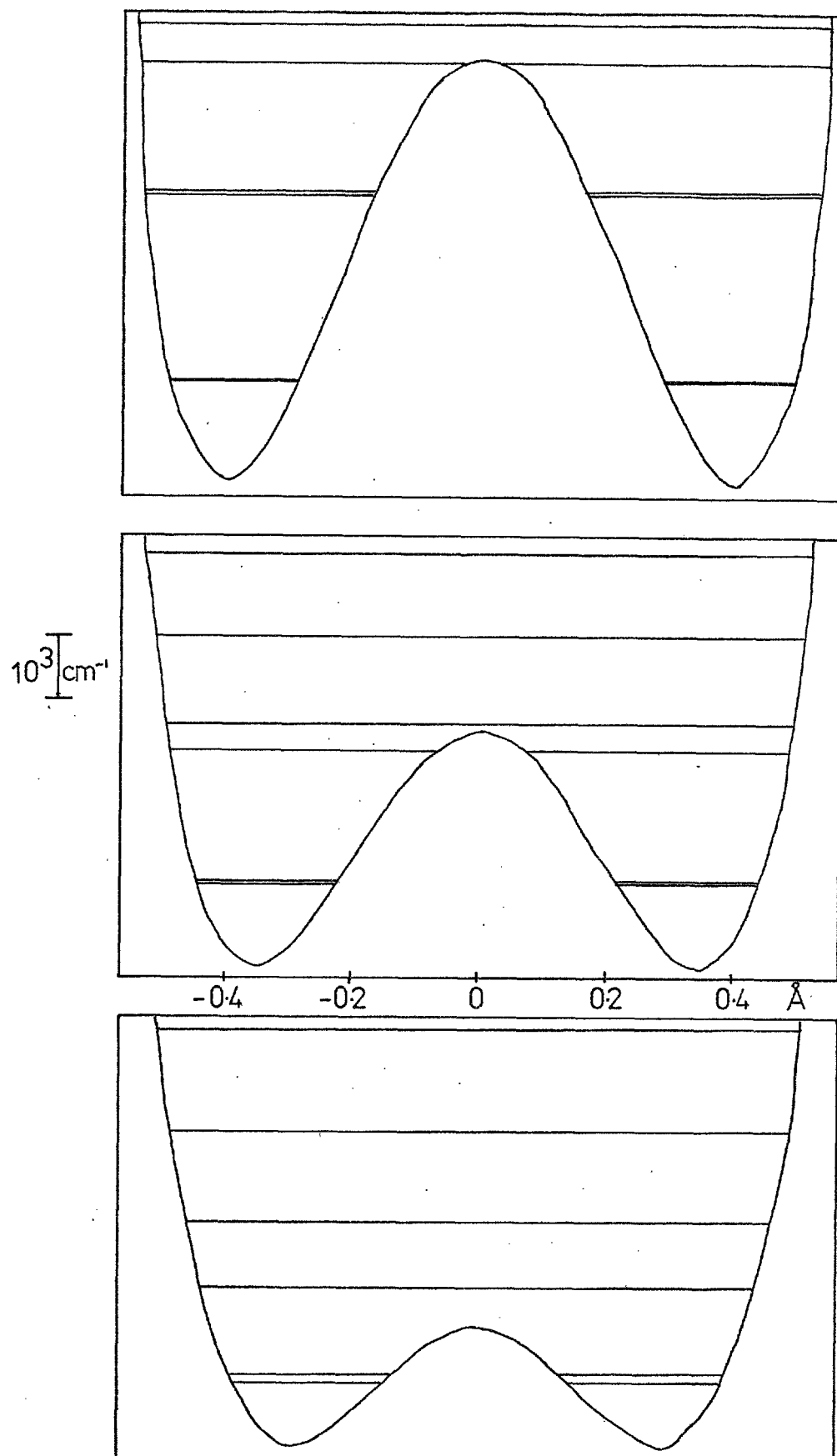


Figure 7.4. Potential functions for $x_0 = 0.40, 0.35$ and $0.30 \text{ \AA}$, with eigenvalues superimposed. The proton case.

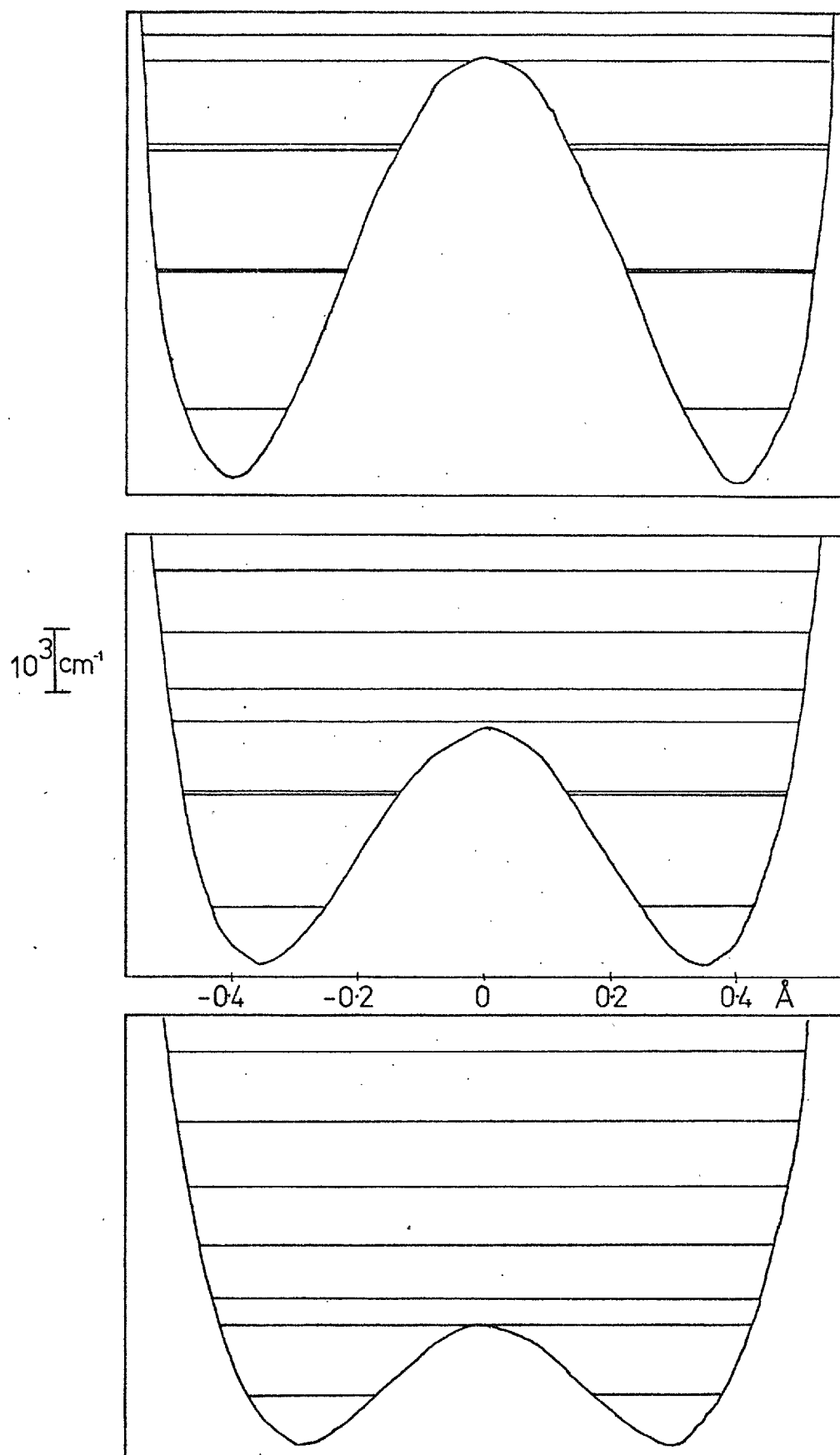


Figure 7.5. Potential functions for $x_0 = 0.40, 0.35$ and 0.30 Å , with eigen-values superimposed. The deuteron case.

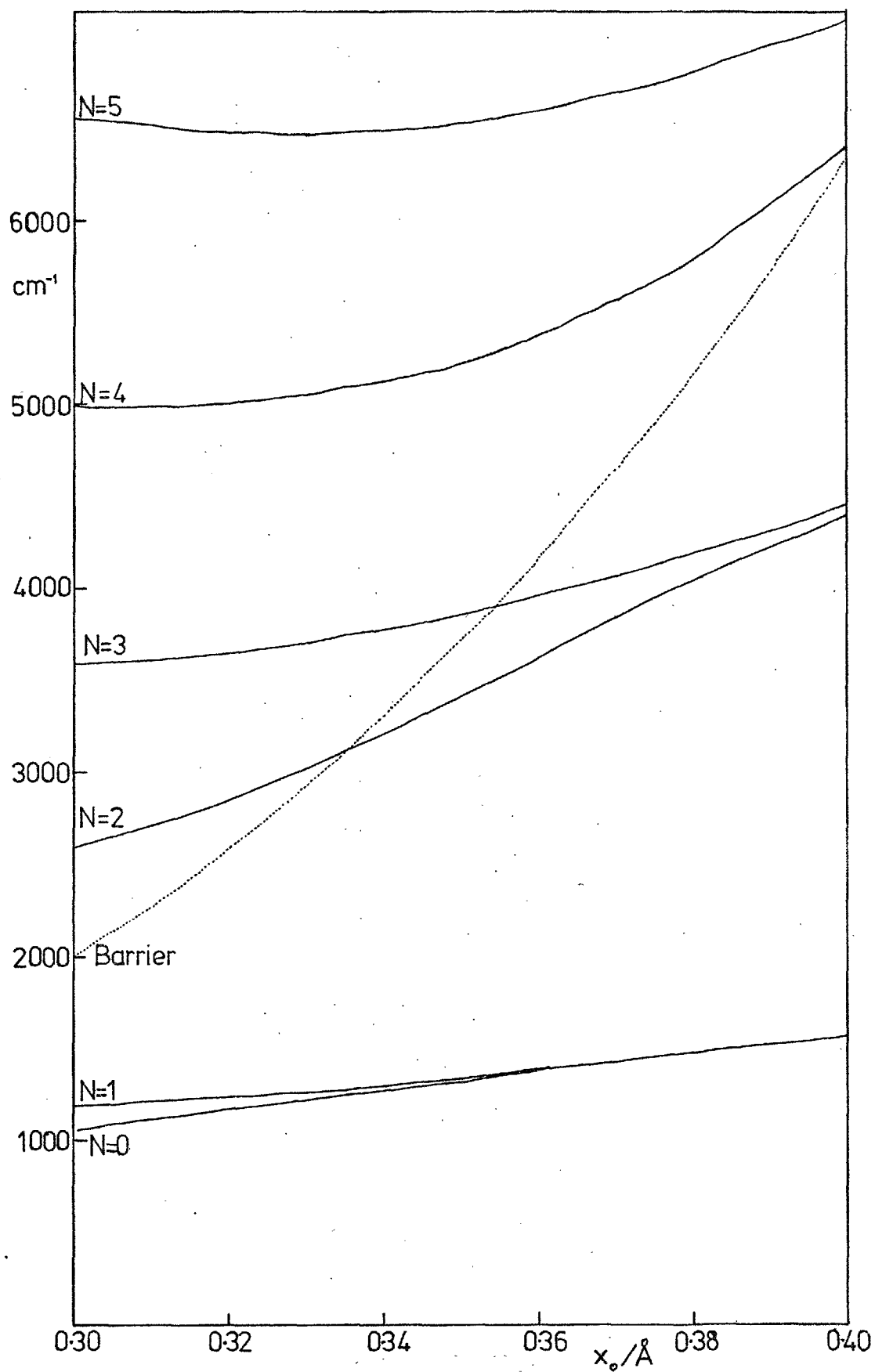


FIGURE 7.6
Evolution of the eigenvalues
in the range of the fluctuations.

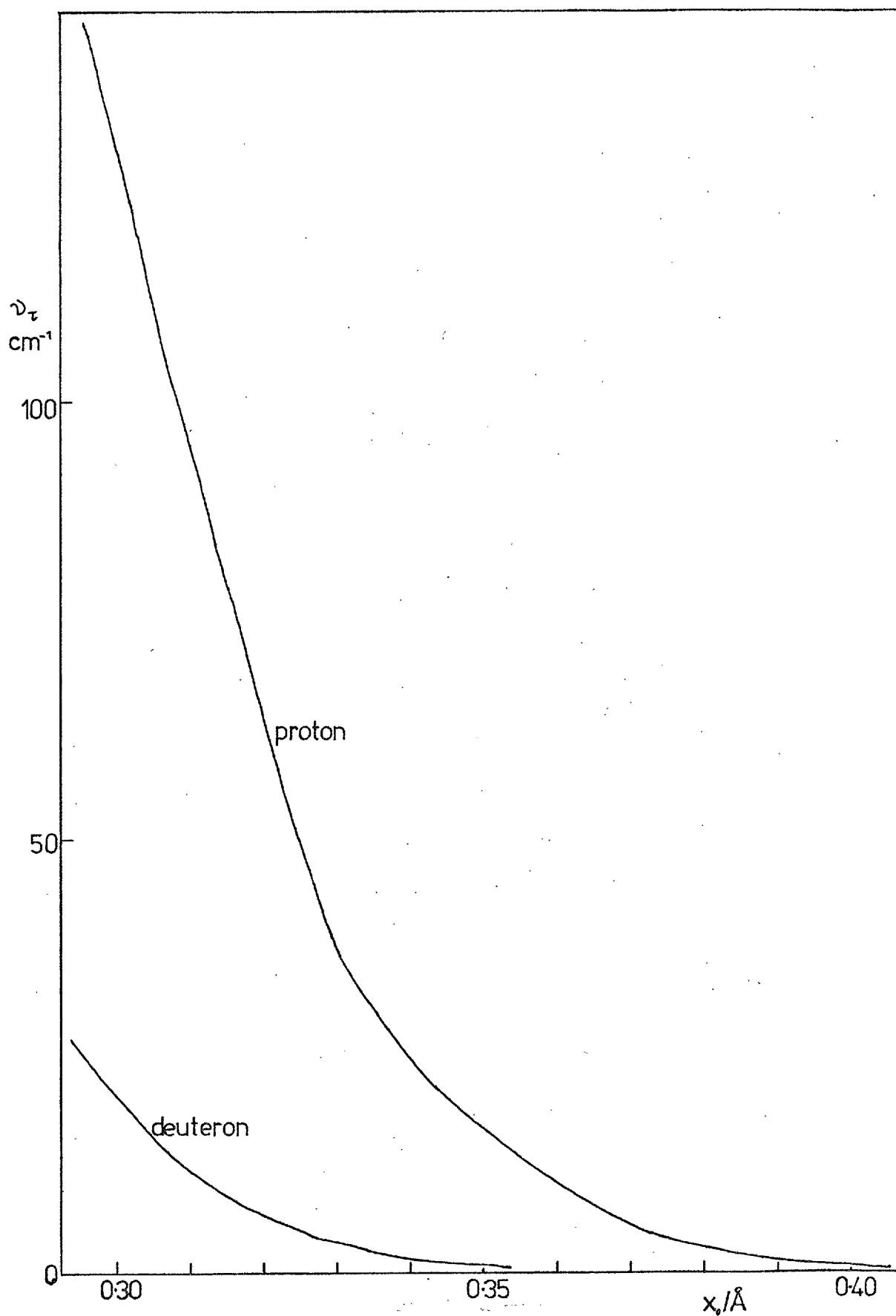


FIGURE 7.7

The tunnelling frequency for various well separations.

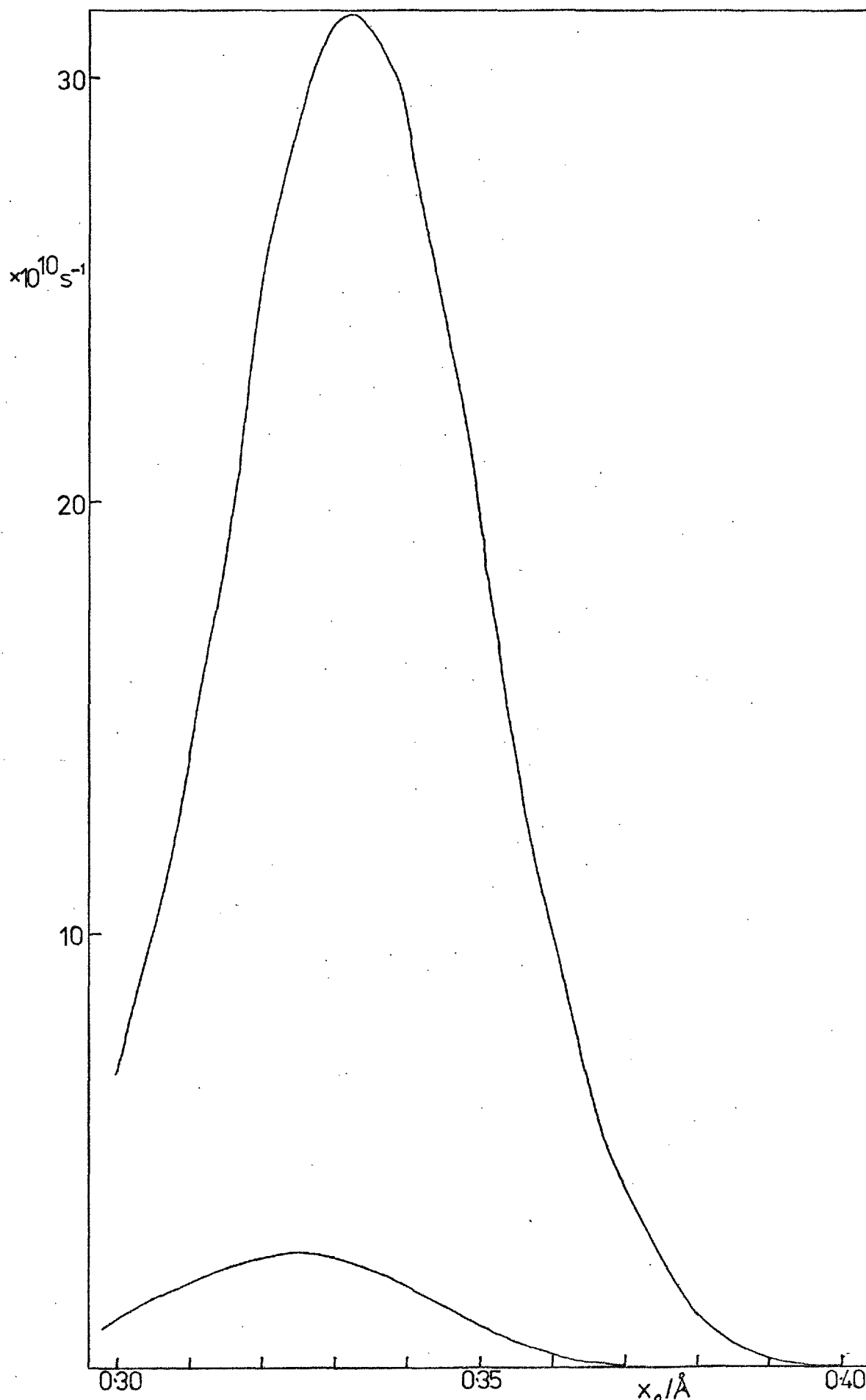


Figure 7.8. Rate of prototropism for various well separations with a variance, $\alpha^2 = 4.0 \times 10^{-4} \text{ \AA}^2$.

The approximate overall tunnelling rate, R , was calculated by averaging the weighted values at the eleven values of x_0 :

$$R = \frac{\sum_{n=1}^{11} (v_{\tau n} \times p(x_0)_n)}{\sum_{n=1}^{11} p(x_0)_n} \quad 7.5$$

$$\text{where } p(x_0)_n = \frac{1}{\alpha\sqrt{2}} \exp \left\{ - \left[\frac{(x_0)_n - 0.35}{\alpha\sqrt{2}} \right]^2 \right\} \quad 7.6$$

It is evident that the introduction of the fluctuating barrier leads to an increase in the overall tunnelling rate, even though the fluctuation is symmetric about the mean barrier. This is clearly due to the increase in $-(\partial v_{\tau}/\partial x_0)$ with decreasing x_0 . Table 7.3 shows the overall tunnelling rate for a variety of distributions of the fluctuations. As the distribution spreads the overall rate increases for both proton and deuteron whilst the ratio $R(H)/R(D)$ falls.

TABLE 7.3 Approximate Overall Tunnelling Rates

Variance (x_0) ($10^{-4} \text{ \AA}^2$)	R(proton) (10^{10} s^{-1})	R(deuteron) (10^{10} s^{-1})	R(H)/R(D)
0	50.1	2.52	20
1.0	55.9	3.23	17
1.56	58.8	3.65	16
4.0	71.9	5.80	12
6.25	80.3	7.31	11

Figure 7.9 shows the rate of tunnelling against the frequency of absorption, ν_{τ} . In order to derive a calculated spectrum from this data it would have to be multiplied by the appropriate frequency, Boltzmann factor and transition factor, $(\langle \psi_0 | x | \psi_1 \rangle)^2$. With increasing frequency (decreasing barrier height), the Boltzmann factor rises (since the transition arises from the lowest state, $N=0$) and the transition factor falls* ⁸³.

7.7 The N-H stretching mode, ν_s

The two transitions $(N=0) \rightarrow (N=3)$ and $(N=1) \rightarrow (N=2)$ are involved here. Because the separation between the levels $(N=0)$ and $(N=1)$ is small both transitions must be considered, however Wood⁸³ has shown that the lower frequency transition has a far greater transition factor than the upper one. The true intensities depend also upon the frequency and Boltzmann factor. No detailed estimation of these values is made here.

Figures 7.10 and 7.11 show the fluctuation probability, $p(x_0)$, against the absorption frequency, for both the protonated and deuterated systems. Of particular interest is the shape of the $(N=0) \rightarrow (N=3)$ band of the protonated complex (figure 7.10). The two levels involved reach a point of closest approach at approximately $x_0 = 0.325 \text{ \AA}$. Consequently the frequency of the transition reaches a minimum of 2460 cm^{-1} , and is then folded back, giving the band its asymmetric appearance.

* The proton results described here lie between $B=4.40$ and 7.85 . Wood's equation 4.8 (p.336) should read:

$V = -ax^2 + bx^4$; comparing this with equation 7.2 gives
 $B = -(a^3/\hbar b^2)^{1/3}$.

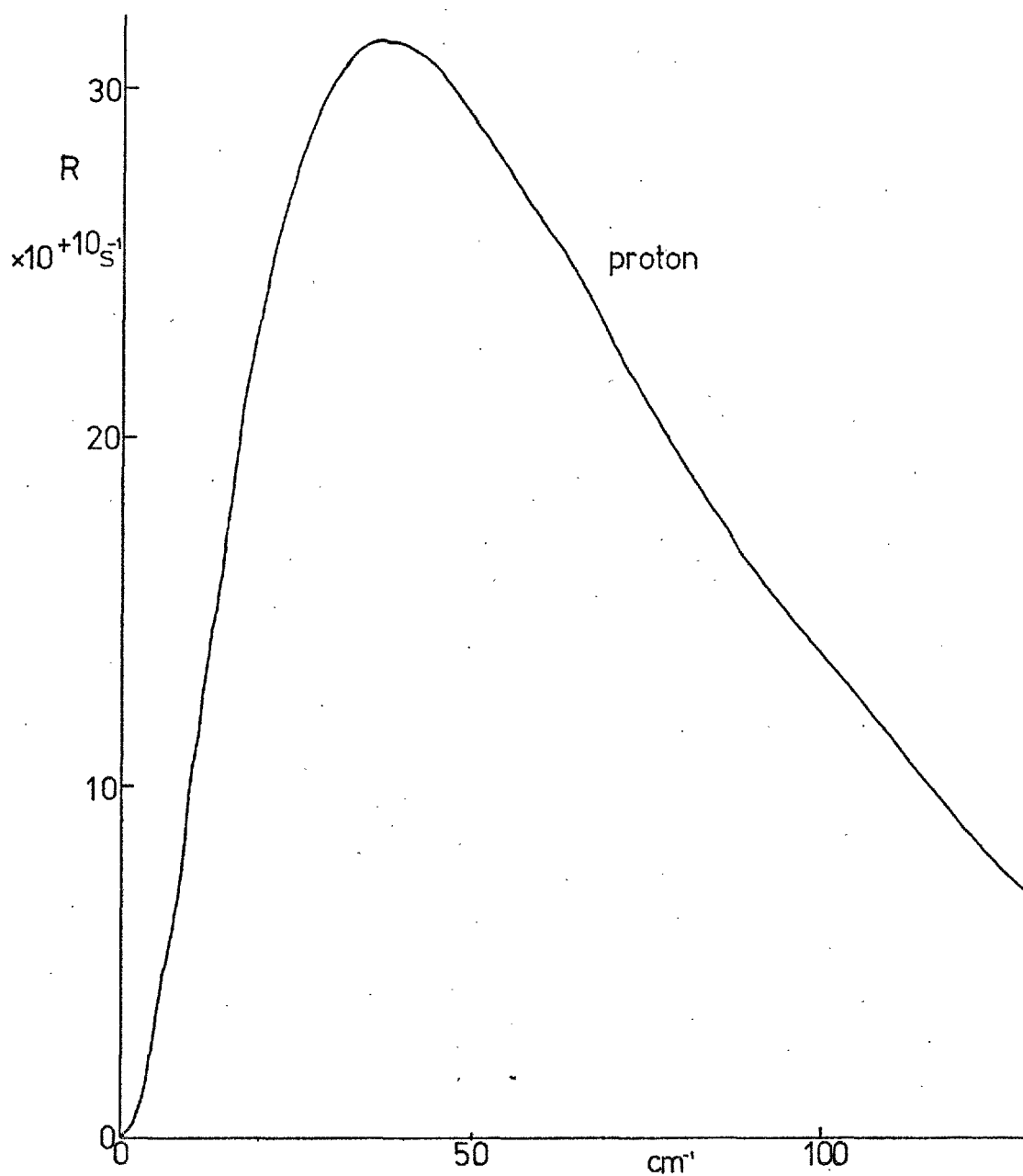
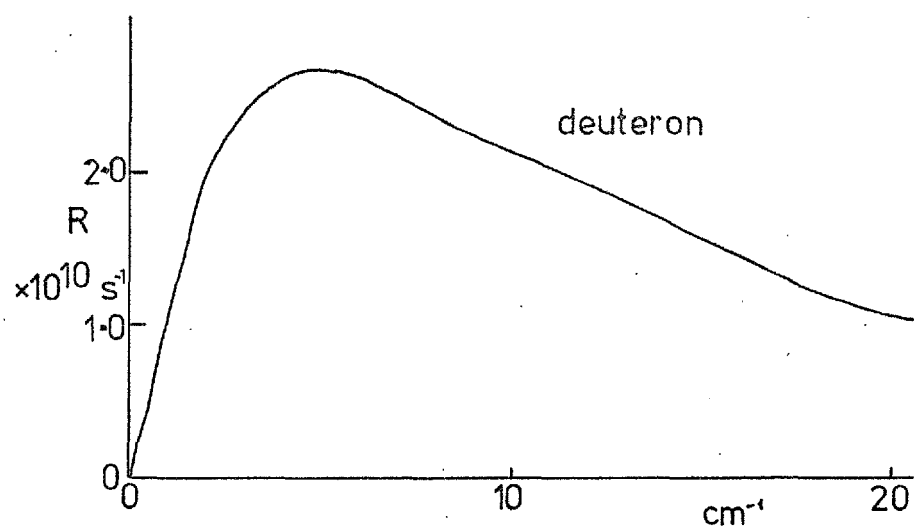


Figure 7.9. Rate of prototropism vs. frequency ;
for well separations with a variance $\sigma^2 = 4.0 \times 10^{-4} \text{ \AA}^2$.

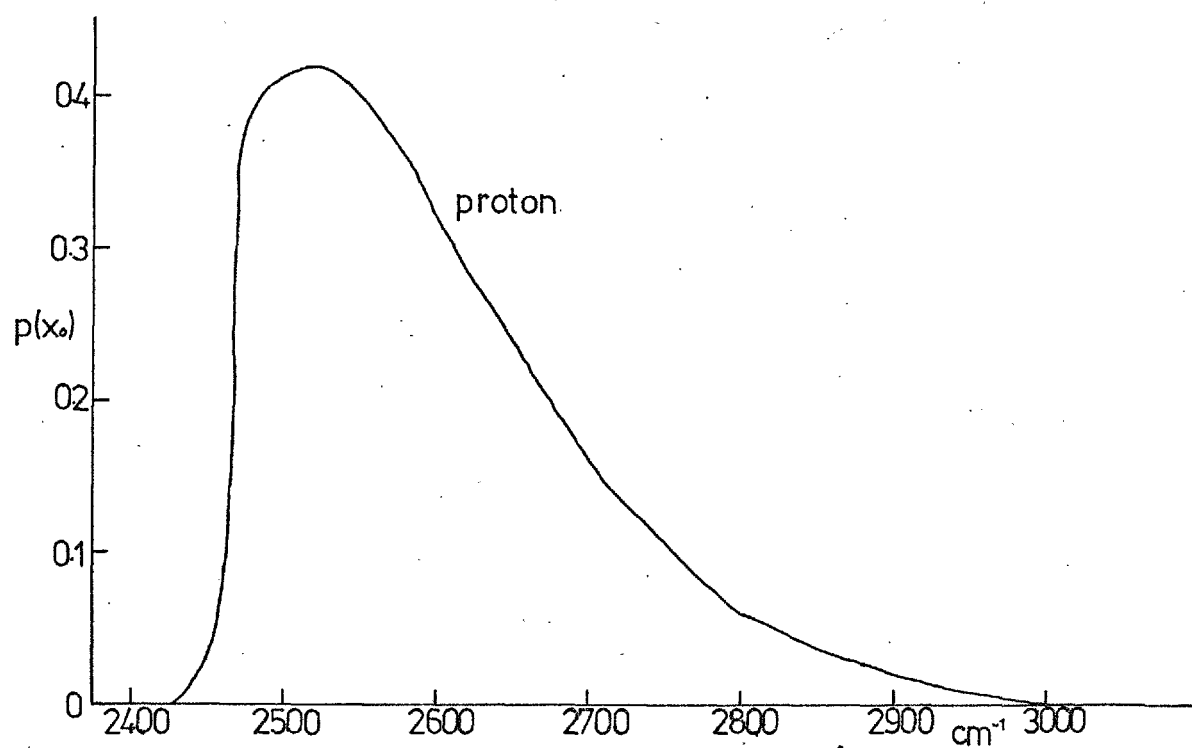
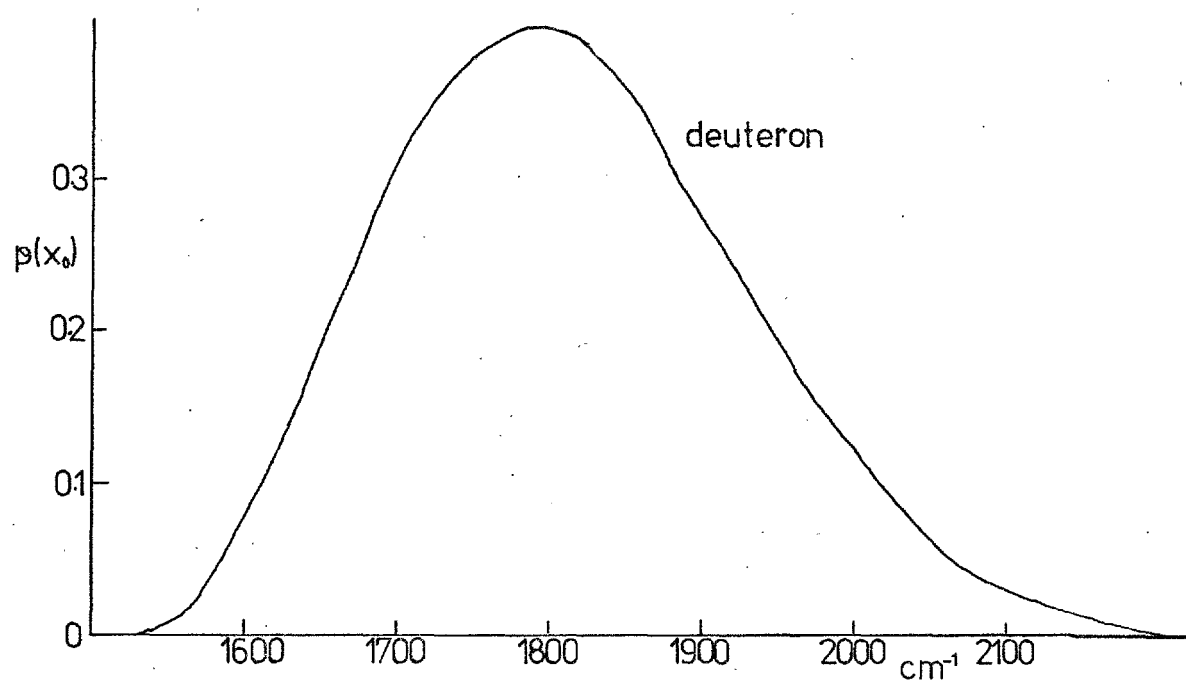


FIGURE 7.10

The upper frequency component ($(N=0) \rightarrow (N=3)$) of $\nu_s \cdot p(x)_0$ vs ν_s .

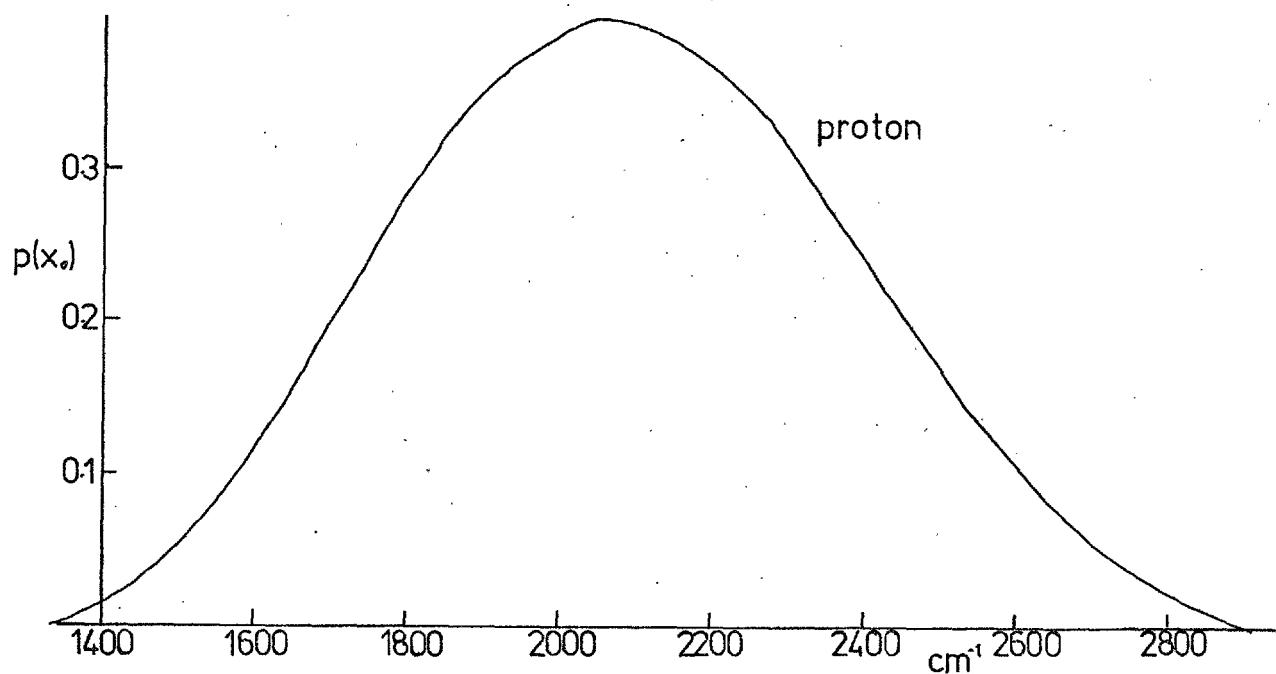
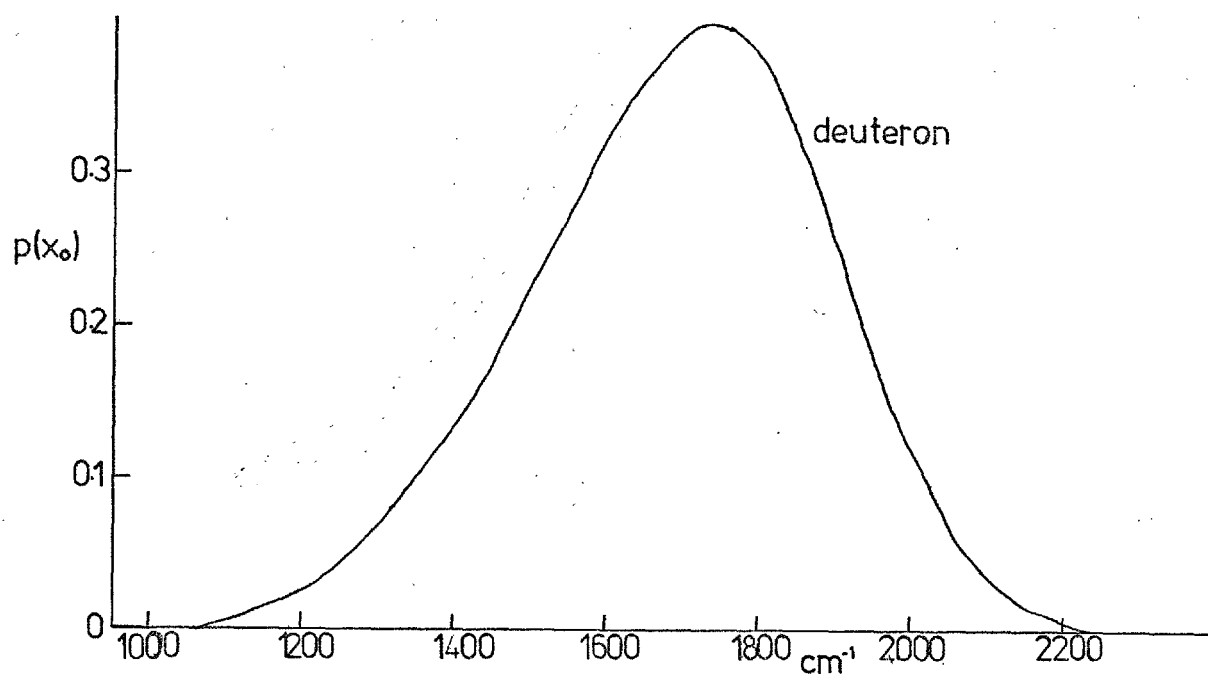


FIGURE 7.11

The lower frequency component $((N=1) \rightarrow (N=2))$ of

$$\nu_s \cdot p(x)_0 \text{ vs } \nu'_s$$

This is an effect which depends upon the initially chosen parameters and cannot be expected to be generally applicable. Were it not for this effect the H-band would be broader than the D-band in $(N=0) \rightarrow (N=3)$ as is the case in the $(N=1) \rightarrow (N=2)$ bands.

The $(N=0) \rightarrow (N=3)$ transition frequency is much less sensitive to the barrier fluctuations than that of the $(N=1) \rightarrow (N=2)$ transition (figure 7.6), consequently the latter's band-width is much greater than that of the former.

7.8 Conclusions

It has been shown by the application of a crude model that the frequencies of the modes most closely associated with the hydrogen bond are extremely sensitive to the N-N separation. This effect is also expected to apply to the internal modes in complexes between polyatomic molecules and ions. The frequency of prototropism is greater than that expected from a static model because of the lowering of the barrier due to the N-N fluctuations. The wide range of tunnelling rates also explains the failure to observe splitting due to tunnelling in the internal modes.

Improvements in this model would require more detailed consideration of the interactions involving the symmetric stretching and bending modes, since the method of calculation employed here makes the invalid assumption of the separability of the different modes. One suggested method is to use Yarwood and Robertson's model⁸² to derive information on ν_{τ} .

CHAPTER 8.

8. THE 3,5 DIMETHYLPYRIDINE SYMMETRIC COMPLEX

8.1 Introduction

Stress has been placed already at several points in this work upon the interest in the crystallisation of symmetric complexes in which the symmetry of the proton potential may be established in an ordered situation. In this chapter studies of one such crystalline complex, that of 3,5 dimethylpyridine (3,5 dimepy), by means of infra-red, Raman and X-ray crystallographic methods are described. It is believed that this is the first such crystallised symmetric complex between pyridine bases to be reported.

Unfortunately, whilst the space group has been identified and accurate cell parameters have been obtained, the arrangement of the cations in the unit cell has not been established. Consequently it has not proved possible to determine the nature of the proton potential. Those facts which can be ascertained from the crystal symmetry and other considerations are discussed here.

8.2 Evidence for the nature of the crystallised species.

Crystals containing the complex cation, (3,5 dimepy₂H)⁺, have been prepared with three counter-ions, perchlorate, fluoroborate and hexafluorophosphate. It is first of the utmost importance to establish that these crystals do contain the complex cation. The evidence is of two kinds:- Infra-red and elemental analysis.

One of the most important characteristics of hydrogen bonded complexes between heterocyclic bases is the pronounced ν_s (N-H stretching) band which appears as a doublet at about 2500 and 2000 cm^{-1} . The free salt on the other hand has a much weaker band around 3100 cm^{-1} . Figure 8.1 shows the ν_s band region for a variety of solid $(3,5\text{-dimepy}_2\text{H})^+$ complexes. The appearance of the spectrum in this region conclusively indicates the presence of complex.

The elemental analyses of a number of compounds are given in table 8.1. Evidently the results tally with the predicted values in all but two cases. The high values for carbon, hydrogen and nitrogen and the low value for phosphorus in $3,5\text{-dimepyH}^+\text{PF}_6^-$ possibly indicate that some complex is present in this sample. The $(3,5\text{-dimepy}_2\text{H})^+ \text{BF}_4^-$ result iia shows a consistent 5% loss in carbon, hydrogen and nitrogen which indicates the loss of free base by evaporation. There is always a strong scent of free base from the complex crystals, even when recrystallised from acetonitrile and dried. The other analyses and the infra-red evidence indicate that the free base which evaporates is from dissociating complex and not from trapped base molecules in crystal lattice.

The possibility of hydrogen bond formation between the cation $3,5\text{-dimepyH}^+$ and the counter-ion may be excluded on stoichiometric grounds, since the base involved is unfunctional. The absence or near absence of hydrogen bonding between the counter-ions involved and amine salts has been reported⁸⁴.

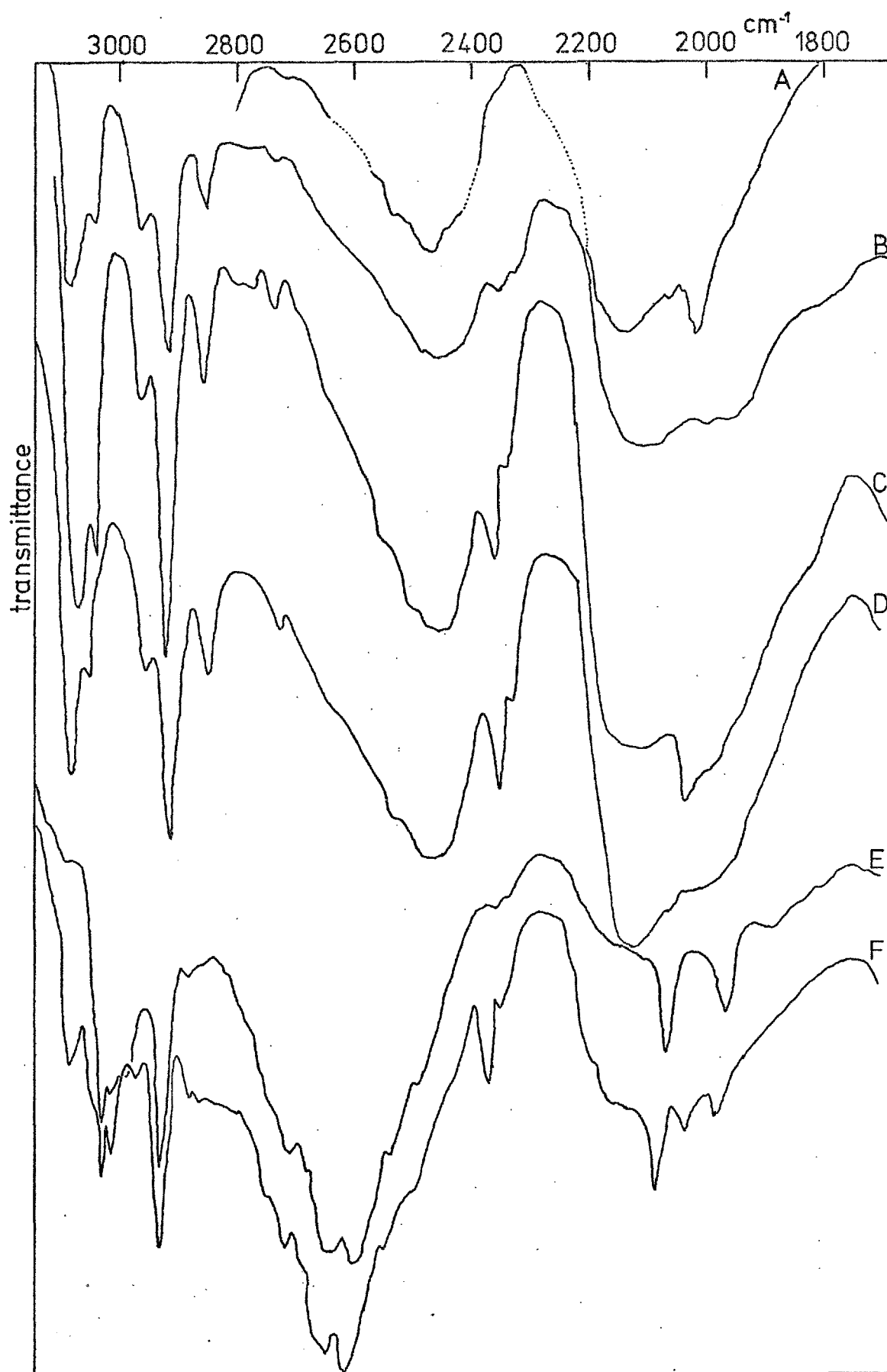


Figure 8.1. The ν_s region of the infra-red spectra of the complex, $(3,5 \text{ dimethylpyridinium})^+$. A: BF_4^- in acetonitrile. B, C, D: BF_4^- , ClO_4^- , PF_6^- in H.C.B.D.mull. E, F: BF_4^- , ClO_4^- in KBr disc.

TABLE 8.1. The Results of Elemental Analyses of Simple and Complex 3,5 dimethylpyridinium salts.

	Carbon %	Hydrogen %	Nitrogen %	Fluorine %	Phosphorus %
3,5 dimepyH ⁺ BF ₄ ⁻					
required	43.13	5.17	7.18	38.98	
found	43.22	5.24	7.12	39.72	
3,5 dimepyH ⁺ PF ₆ ⁻					
required	33.22	3.98	5.53		12.24
found	38.93	4.71	6.54		8.32
(3,5 dimepy ₂ H) ⁺ BF ₄ ⁻					
required	55.65	6.35	9.27	25.75	
found i	55.64	6.37	9.13	- ^a	
found ii	55.77	6.49	9.04	-	
found iia ^b	52.60	6.09	8.68	-	
found iii	54.31	6.20	8.79	-	
(3,5 dimepy ₂ H) ⁺ PF ₆ ⁻					
required	46.67	5.32	7.78		8.60
found	45.91	5.24	7.83		9.08

- a No satisfactory fluorine analysis could be performed for a 3,5 dimethyl pyridine complex system.
- b Analysis iia was performed on the same sample as ii, but after a six week period stored in a sealed container. The C, H and N analysis are each down by 5% indicating the loss of free base by evaporation.

8.3. The crystal structure of the complex
 $(3,5 \text{ dimepy}_2\text{H})^+ \text{BF}_4^-$

The complex crystallises in the triclinic system. The cell parameters are given in table 8.2. These were determined from least square refinement of 29 high-angle reflections measured on a diffractometer using Cu-K radiation. The photographs indicated a centric structure and hence the space group $\overline{P}1$. This was later confirmed by intensity statistics from the full data set. The density of the crystals was determined by flotation to be approximately 1.2 g cm^{-3} . This figure cannot be ascertained more accurately since the crystals have a tendency to decompose and are soluble in the liquids used. However for a molecular weight of 302 and unit cell volume of $1209 \text{ \AA}^3$ this figure implies three formula units per cell.

TABLE 8.2. The cell parameters for the crystal structure of $(3,5 \text{ dimepy}_2\text{H})^+ \text{BF}_4^-$.

<u>a</u>	=	11.612(1) $\text{\AA}$	α	=	92.80(1) $^\circ$
<u>b</u>	=	12.319(1) $\text{\AA}$	β	=	102.18(1) $^\circ$
<u>c</u>	=	8.997(1) $\text{\AA}$	γ	=	104.76(1) $^\circ$
<u>U</u>	=	1209 $\text{\AA}^3$			

The normal complement for $\overline{P}1$ is two, therefore in the general case in order to fit three molecules into the cell at least one must be lying in a special position across a centre of symmetry. The other two may then both be either in special positions or in symmetry-related general positions. For the purpose of further discussion

these two possibilities, which are illustrated in two dimensions in figure 8.2, are labelled A and B respectively. In the figure each molecule is denoted by two half molecules (e.g. δ -g).

If the disposition of the cations in the cell is considered first, it is clear that at least one must have a centre of symmetry. Therefore the hydrogen bond in that one unit must itself be centrosymmetric, either with a single or double minimum. In the latter case the proton will be averaged between the two minima. McGaw and Ibers⁸⁵ have drawn attention to the difficulty of distinguishing between these two proton potential types by crystallography since the sum of the scattering densities for the two half-hydrogens in the double minimum case is only marginally different from the density in the single minimum case. It is however possible to exclude any type of asymmetric potential for this hydrogen bond. Only a knowledge of the N-N distance ($R(N-N)$) would enable the nature of the potential to be established. If $R(N-N) \ll 2.8 \text{ \AA}$ the potential probably has a single minimum whilst a double minimum could be fitted into a larger $R(N-N)$.

The other two complex cations will have centrosymmetric potentials in case A, but in case B, where the two remaining cations are related to each other by a centre of symmetry an asymmetric potential could be found. In figure 8.2 therefore the molecule denoted μ -n may or may not be centrosymmetric.

The placing of the tetrahedral fluoroborate anion is more difficult because it has no centre of symmetry

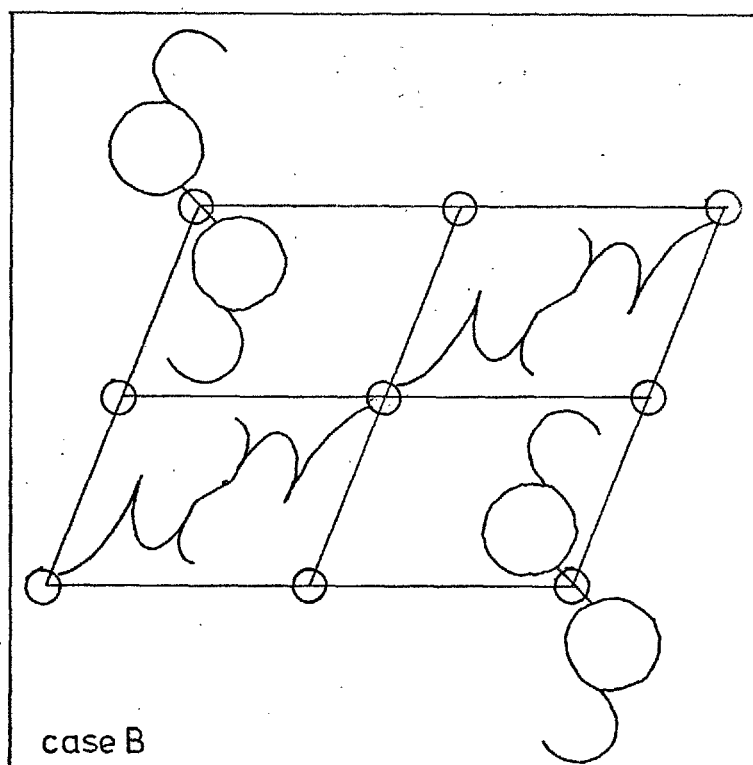
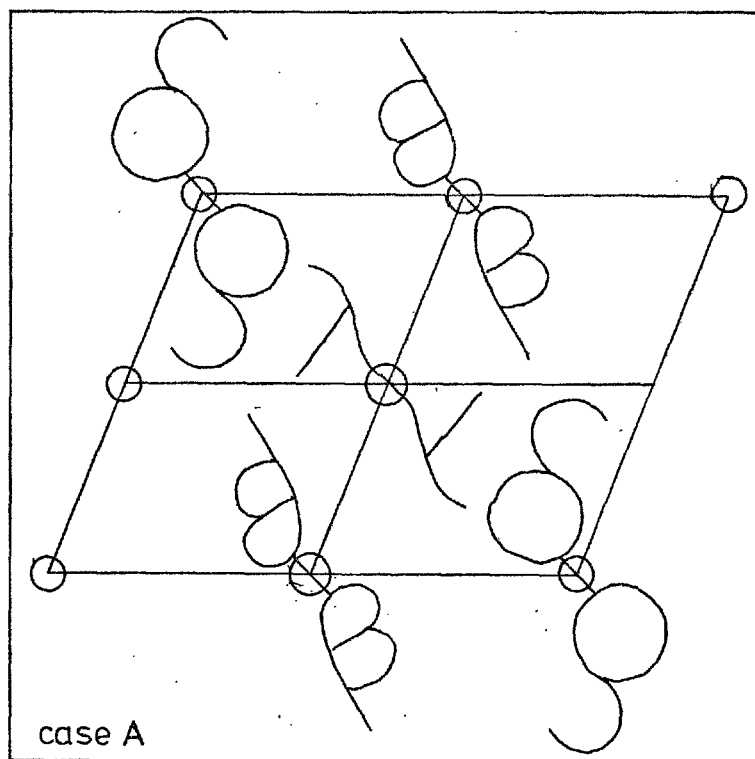


Figure 8.2. The disposition of six half-units in the $P\bar{1}$ space group illustrated in two dimensions. In case A the three units are each in special positions. In case B the two $\mu - \pi$ units are in symmetry-related general positions, a centre of symmetry between the two half-units is not necessary. $\bigcirc$ represents a centre of symmetry. Each unit may represent a $(3,5 \text{ dimepy}_2\text{H})^+$ or BF_4^- ion.

itself. Since at least one anion must be placed upon a centre of symmetry it must be disordered. It is unlikely that the fluoroborate anions are disposed as in case A since this requires all three anions to be disordered. It is therefore suggested that the two remaining anions are placed in general positions.

No firm conclusion can be drawn about the placing of the cations, but case B seems more likely in view of the limitation which the location of all the cations on centres of symmetry imposes. The photographs indicate the possibility of some disorder in the structure. This may not be due just to the fluoroborate anions but to a more serious "misarrangement" of the dimethyl-pyridine molecules throughout the crystal. One such possibility is that the crystal contains some linear coplanar arrangements of cations in which the back-to-back separation of the pyridine rings replaces the hydrogen bond (figure 8.3). Alternatively a slight misorientation of chains may exist throughout the structure.

Attention has already been drawn to the unstable nature of the crystals with respect to evaporation of free base. A similar problem was encountered by Lee and Wallwork⁸⁶ in the only known crystallographic study of a hydrogen bonded dimethylpyridine complex - that between urea and the 2,6 isomer. The present crystals are quite stable when stored in a sealed container since a positive vapour pressure of free base is established and prevents further decomposition. Unfortunately it has not proved possible to perform crystallographic studies under such conditions.

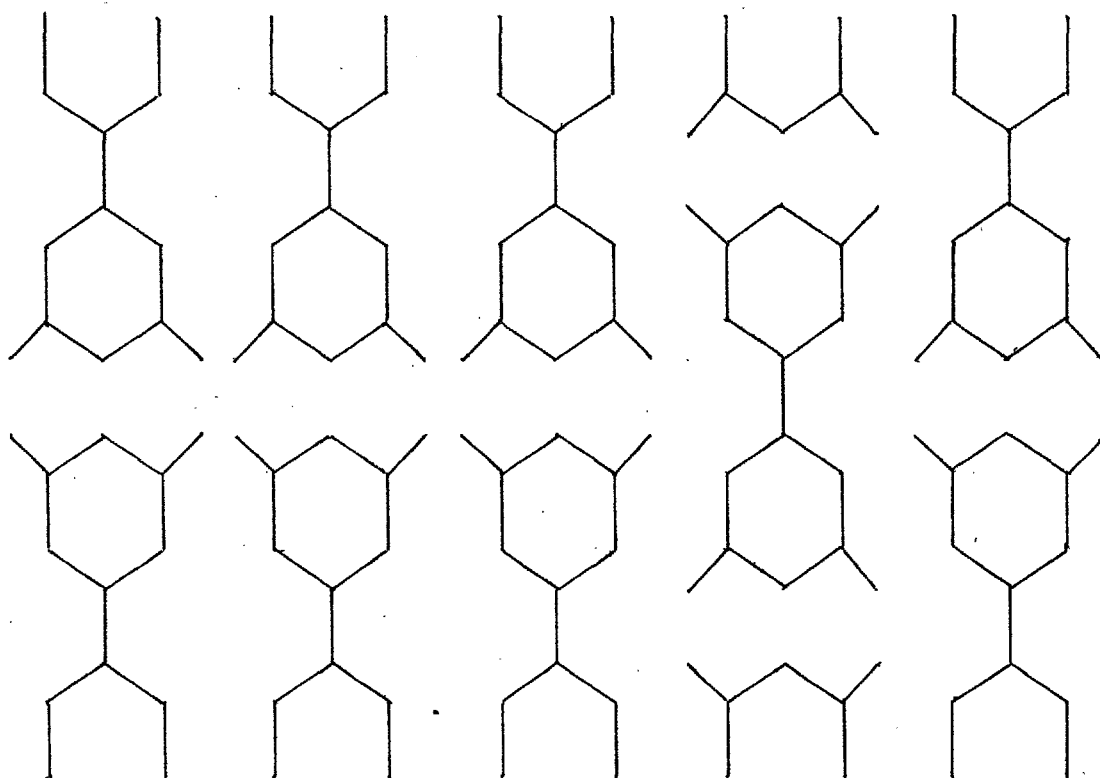


FIGURE 8.3

A possible source of "misarrangement" in the crystal.

A total of three crystals, each coated with picture varnish, was used to determine accurate lattice parameters and to collect full three-dimensional data. A total of 3607 reflections were measured, to $\theta(\text{Cu}) = 60^\circ$, on a Siemens off-line four-circle diffractometer. Numerous attempts to solve the structure using both multiple solution tangent refinement and multiple symbol symbolic addition have failed to give any intelligible structure solution. The reasons for this are as yet unknown and further attempts are being made to resolve these difficulties. It is hoped that the disorder and decomposition problems discussed earlier are not the cause of the present failure.

8.4 The Infra-red and Raman spectra of the complex.

8.4.1. Previous studies of 3,5 dimethylpyridine.

The infra-red and Raman spectra of the free base have been reported by Medhi⁸⁷ and by Green, Harrison, Kynaston and Paisley⁸⁸. In view of the fact that the base attacks all the materials available as cell windows (NaCl, AgCl and KBr crystals) it has not been possible to obtain the infra-red spectrum of the base. The data of Green et al. has been used throughout. Raman data obtained for the base is in satisfactory agreement with that of Green et al.

No attempt has been made to assign frequencies to specific modes. Both Medhi and Green et al. used different assignments (due to Wilson⁸⁹ and to Long and Thomas⁹⁰ respectively). Whilst the former assignment corresponds to that used elsewhere in this work the discrepancies are sufficiently numerous to prevent its acceptance.

No far infra-red spectra are reported in this chapter since no satisfactory results could be obtained

8.4.2 Observations in the ν_s region

In free 3,5 dimepyH⁺ cations this mode appears, as in other pyridine salts, in the region of 3300 cm⁻¹. As has already been mentioned, the complex cation exhibits the characteristic doublet, independent of counter-ion (figure 8.1). It is however clear that the upper frequency band is sensitive to the method of treatment of the sample. In H.C.B.D. mulls it appears at 2460 cm⁻¹ whilst

in KBr discs it is some 160 cm^{-1} higher. The second component has a maximum around 2120 cm^{-1} although various additional sharp peaks contribute at lower frequencies. In solution, the upper ν_s peak resembles that in the mull whilst the lower peak is at 2150 cm^{-1} . The solution results agree with those of Dean⁹¹, who observed that the upper frequency peak (2600 cm^{-1}) was weaker than the lower frequency peak (2100 cm^{-1}). The strength of the latter was attributed to a combination band.

8.4.3 Observations in the Internal Mode Region

Consolidated data from the base⁸⁸, crystalline salt and crystalline complex are presented in tables 8.3 and 8.4. There are marginal differences between samples containing different counter-ions. These are mostly in the intensity of the observed bands although some bands are unobserved with one counter-ion. Data obtained from samples with three different counter-ions have been collated in table 8.3 in order to show the origin of the complex bands in the spectra of the components.

There are pronounced differences between the spectra obtained from samples in nujol mull and those in KBr disc. Attention has already been drawn to the effect of the medium upon the ν_s band. There was no profound deviation observed in the spectra of samples in acetonitrile solution. Since solvent bands obscured parts of the region of interest and no detailed study of solutions was made, no report is made here.

Evidence for the absence of the free components from the complex samples is abundant. Strong base bands

TABLE 8.3. The composite Infra-red and Raman spectra of the complex cation, $(3,5 \text{ dimepy}_2\text{H})^+$ and of the free salt and base for comparison.

(Counter-ion bands have been omitted; frequencies are in cm^{-1})

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺			
infra-red	Raman	infra-red		Raman	infra-red		Raman
		<u>mull</u> ^b	<u>disc</u>		<u>mull</u> ^b	<u>disc</u>	
			1622 w	1626 w	1630 m	1629 m	1627 m
					1618 w		1621 m
1602 s	1599 s	1597 s	1597 vs	1602 m			
1581 vs	1579 s						
		1561 m	1565 s		1565 s	1570 s	
			1473 s	1474 vw		1470 s	
1463 vs	1452 m		1463 s				
			1450 sh			1453 sh	
1426 vs	1432 m		1440 sh				
		1393 vw		1393 m	1396 s		1404 m

a : data of Green et al⁸⁸.

b : nujol mull; nujol absorbs in the regions 1480-1410 and 1380-1350 cm^{-1} .

Contd.

TABLE 8.3. Continued : 2

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺		
infra-red	Raman	infra-red	Raman	infra-red		Raman
		<u>mull</u> ^b	<u>disc</u>	<u>mull</u> ^b	<u>disc</u>	
			1386 m	1389 m	1389 m	1394 w
1379 s	1380 s		1378 w			
1358 sh,m		1364 vw	1363 vw			
			1347 m		1349 m	
		1327 w	1327 w		1326 w	
1320 m	1322 vw		1322 m	1320 w	1321 m	1323 vw
			1302 m			
			1297 m			
			1293 m	1289 m	1294 w	1290 w
		1286 m				
1273 w	1270 s	1273 m	1275 m			
		1267 m	1264 s	1269 s	1268 m	1275 w
1232 s	1234 vw	1251 w	1250 w			

TABLE 8.3. Continued : 3

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺		
infra-red	Raman	infra-red	Raman	infra-red	Raman	
		<u>mull</u> ^b <u>disc</u>		<u>mull</u> ^b <u>disc</u>		
1164 vs	1166 m	1168 m 1167 m	1170 vw			
		1152 m 1150 m		1146 m 1141 m		1145 w
1138 s	1139 m	1136 m 1136 m	1137 vw			
				1114 sh 1109 w		1109 w
		1055 s 1055 s		1057 m 1055 w		
1043 sh,s			1041 s			1037 s
1032 s	1032 vs			1028 m 1026 w		
1011 m		1012 m 1015 m	1009 vw			1014 w
				994 w 990 br,w		
				950 m 950 br,w		
994 w		938 sh 943 w	940 vw			
				933 w		

TABLE 8.3. Continued : 4

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺	
infra-red	Raman	infra-red	Raman	infra-red	Raman
		<u>mull</u> ^b <u>disc</u>		<u>mull</u> ^b <u>disc</u>	
929 w	935 m	930 w 929 w			
		917 w	911 w		
		868 m 867 w			
857 vs	864 vw	859 m 858 s		816 vs	
		777 w 771 vw		765 w 762 sh	
		751 s 751 s	754 m		
		740 w 741 w		738 m 738 s	
			731 w	727 m 730 w	732 vs
727 sh,m					
				719 w 724 w	
715 vs	719 vs	714 w 714 w			
710 vs					
		702 m 702 sh		709 br,w	
		697 m 697 s	690 w		

TABLE 8.3. Continued : 5

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺	
infra-red	Raman	infra-red	Raman	infra-red	Raman
		<u>mull</u> ^b 681 s	<u>disc</u> 681 vs	<u>mull</u> ^b 679 s	<u>disc</u> 679 s
			626 m		645 w
				605 w	
				577 w	
				568 w	
		555 br,m	554 br,m		
				546 w	
539 m	537 s	535 w	532 m		
532 m				532 w	531 w
					537 s
			525 w		526
			514 w		510 w
498 w	498 m	501 m	503 w		
		474 w	481 w	476 s	479 s
			478 vw		
			462 m		
438 w	441 w	439 m	440 m		

TABLE 8.3.

Continued : 6

3,5 dimepy ^a		(3,5 dimepy ₂ H) ⁺		3,5 dimepyH ⁺	
infra-red	Raman	infra-red	Raman	infra-red	Raman
		<u>mull</u> ^b <u>disc</u>		<u>mull</u> ^b <u>disc</u>	
395 w	397 vw	428 w		432 m 433 m	
			281 m		355 w
272 m	274 vs		243 m		282 m
	233 vs		212 m		247 m
					212 m

TABLE 8.4.

The infra-red spectra of the complex cation, $(3,5 \text{ dimepy}_2\text{D})^+$ and of the free salt and base for comparison. (Only fluoro-borate^a counter-ions used; frequencies in cm^{-1})

$3,5 \text{ dimepy}^b$	$(3,5 \text{ dimepy}_2\text{D})^+$	$3,5 \text{ dimepy D}^+$	
	mull ^c	mull ^c	disc
	1625 w	1623 w	1623 w
		1606 m	1606 m
1602 s	1596 s		
1581 vs			
	1564 s	1565 m	1572 s
		1558 m	
	1495 sh	1494 s	1496 s
1463 vs		1465 ?	1472 m
1426 vs			
			1396 sh
	1395 w	1395 s	1392 s
1379 s	1383 w		
1358 sh,m			
			1348 w
1320 m	1329 w		1323 w
			1298 s
	1288 m	1290 s	
	1284 sh		1285 m
1273 w	1273 sh		
	1268 m	1267 m	1271 w
	1251 sh		
1232 s			
	1177 sh		
1164 vs	1166 m		
944 w			
929 w	931 w		920 w
		895 m	893 m
	868 m	875 w	877 w
857 vs	859 m		857 sh
			843 s

Contd.

TABLE 8.4. Continued : 2

3,5 dimepy ^b	(3,5 dimepy ₂ D) ⁺	3,5 dimepy D ⁺	
	mull ^c	mull ^c	disc
	815 s	810 m,br	813 m,br
			771 w
	752 s		763 w
727 sh,m	727 w	727 w	725 m
715 vs		715 w	
710 vs	702 m		709 m
	697 m		697 vs
	684 sh	679 s	677 m
	679 s	666 m	666 sh
	560 br,m		
593 m			
532 m	526 w		532 m
498 w			
438 w	431 w		434 m
			418 m
			410 m
395 w			394 m
			356 w

a : fluoroborate absorption: 1250 - 960 and 520 cm⁻¹.

b : data of Green et al⁸⁸.

c : nujol mull; nujol absorbs in the regions 1480-1410 and 1380-1350 cm⁻¹.

at 1581, 1426, 1032 and 710 cm^{-1} and strong free salt bands at 1396 and 816 cm^{-1} are clearly absent. In only a small number of cases has it not been possible to link a complex band with a frequency due to one or other of the free components. In the vast majority of cases the absolute shift in frequency between the free component and the complex is less than 5 cm^{-1} ; and only in three cases is the shift more than 10 cm^{-1} .

8.5 Discussion

Until the conclusive result of the X-ray crystallographic study is obtained deductions on the 3,5 dimethylpyridine complex must necessarily be tentative. The base is strong enough for the possibility of a short, single minimum hydrogen band to be included. However the observation of a ν_s massif similar in structure to that of other symmetric^{69,92} and asymmetric⁷⁴ pyridine complexes, and the assignment of acceptor- and donor-like bands in the internal mode region suggest that a double minimum of some description would be more appropriate. The origin of the large number of observed internal modes in the presence of complex molecules at two or three different locations in the crystal lattice may be conclusively rejected upon the grounds that the acceptor and donor assignment is satisfactory. The splitting is then due to the distinction between the acceptor and base moieties.

Differences are to be expected in the spectra of crystals containing different counter-ions since the crystal symmetry constraints are likely to be different and the proton potential is extremely sensitive to the

field imposed by the counter-ions and the symmetry.

The sensitivity of the spectra to the nature of the sample is surprising - particularly in the ν_s region. Generally the weaker the base, the higher is the value of ν_s in symmetric complexes in solution. However the ranges for the two peaks are very narrow^{69,92}: 2500-2530 and 2055-2145 cm^{-1} . Solution results for the present system are, at 2460 and 2150 cm^{-1} , marginally outside these limits. Naturally no other data for symmetric crystalline complexes of the pyridine-type exist; therefore no direct comparisons may be made. The only feasible explanation at present seems to be that the compression of the crystals in the making of the KBr disc somehow alters the structure. Possibly the micro-crystals reach a preferred orientation upon compression. A more unlikely suggestion is that nujol leaches free base out of the crystal structure of the mull sample; however 3,5 dimethylpyridine is polar and insoluble in paraffin oil. Furthermore certain free base bands are definitely absent.

The pattern of frequencies observed in the internal mode region of the complex spectrum shows that extra frequencies are introduced in making the sample into a disc, or that frequencies are lost in the mull sample. These frequencies are not exclusively either acceptor- or donor-like bands. Comparison with the Raman spectrum, which is of pure sample ground with a pestle and mortar, is of no assistance since frequencies unique to both mull and disc samples appear in the Raman.

No splitting of internal modes due to proton tunnelling is observed, presumably because of the wide range of values of ν_{τ} described in the previous chapter.

8.6 Conclusions

It is evident that the 3,5 dimethylpyridine complex merits further investigation. The direction such investigation might take would depend upon the outcome of further crystallographic studies. One obvious line of attack would be to examine such anisotropic properties as the crystal possesses. If the unusual ν_s results are due to a preferred orientation then this could be detected. Similarly the directional nature of proton tunnelling might be used in some way in its evaluation.

The evidence of frequencies characteristic of the free donor and acceptor in the complex crystal is evidence of a double minimum in the proton potential. Further studies should be able to ascertain the dimensions of the potential wells.

CHAPTER 9.

9. SOME STUDIES OF ^{15}N ENRICHED PYRIDINE

9.1. Introduction

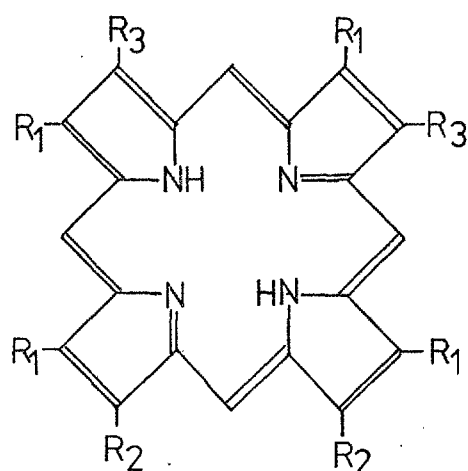
In this chapter n.m.r. (both ^1H and ^{15}N) and Raman spectra of ^{15}N enriched pyridine are reported. It had been hoped that results of ^{15}N n.m.r. experiments upon the hydrogen-bonded complex might give further insights into the nature of the proton potential. For example, in line with previous results, line splitting or broadening due to the instantaneous non-equivalence of the nitrogens might be expected. However instrumental difficulties and the failure to observe an intelligible ^{15}N signal from pyridinium ions under various conditions have prevented completion of this work.

Mention was made in section 2.4 of the complications caused in both proton and ^{14}N n.m.r. by the electric quadrupole of the ^{14}N nucleus. ^{15}N , with a spin of $\frac{1}{2}$, possesses no such quadrupole and presents no such inherent problems in n.m.r., excepting its low natural abundance (0.365 atom %). Although ^{15}N n.m.r. studies can, in principle, be carried out with natural abundance ^{15}N samples this does require high magnetic fields for high sensitivity. In addition the present study requires complex molecules containing two ^{15}N nuclei and this is only possible with an enriched sample. For these experiments 96.9 atom % ^{15}N pyridine was supplied (Prochem) in a sealed 5 mm o.d. n.m.r. tube.

9.2 ^{15}N n.m.r. studies

Previous ^{15}N n.m.r. studies on enriched pyridine have been carried out by Chuck⁹³, Price⁹⁴ and Lichter and Roberts⁹⁵. In each case proton decoupled spectra were run. As well as neat pyridine, solutions in methanol and in trifluoroacetic acid and of the hydrochloride in methanol have been examined. The pyridine resonance occurs at approximately 290 p.p.m. downfield from $^{15}\text{NH}_4^+$. Of particular relevance to the present work is the 110 p.p.m. shift upfield which occurs upon protonation⁹⁵ (pyHCl in methanol). At the 6.08 MHz used by Lichter and Roberts this represents a shift of 668 Hz. Coupling between ^{15}N and the N-H proton has not been measured, however ^{13}C - ^{15}N and ^1H - ^{15}N coupling constants have been derived from ^1H and ^{13}C n.m.r. spectra and used⁹⁵ to estimate the degree of protonation or of hydrogen-bonding in methanol solution. Naturally there would be especial interest in such measurements upon solutions known to contain $(\text{py}_2\text{H})^+$. The large ^{15}N resonance shifts also make it possible to distinguish the three species (py, pyH^+ and (py_2H^+)) in principle.

The ^{15}N n.m.r. spectra of enriched $^{15}\text{N}_4$ -protoporphyrin-IX dimethyl ester (I) (figure 9.1) and $^{15}\text{N}_4$ -coproporphyrin-III tetra-methyl ester(II) have provided evidence⁹⁶ of the nature of the internal hydrogen bonding. At -60°C the rate of tautomerism is slow enough for two distinct nitrogen signals characteristic of pyrrole and pyridine, respectively weakly and strongly hydrogen bonded, to be observed. A pair of asymmetric $\text{NH}\cdots\text{N}$



protoporphyrin-IX methyl ester

$R_1 = -CH_3$

$R_2 = -CH_2CH_2CO_2CH_3$

$R_3 = -CH=CH_2$

coproporphyrin-III methyl ester

$R_1 = -CH_3$

$R_2 = R_3 = -C_6H_5$

octaethylporphyrin

$R_1 = R_2 = R_3 = -C_2H_5$

Figure 9.1 : Porphyrin structures.

hydrogen bonds is deduced. Warming the samples alters the proton spectrum to that consistent with a time-averaged interaction between an inner proton and the four ^{15}N nuclei. Arrhenius plots indicate the possibility of proton tunnelling with rates derived from the p.m.r. data ranging between 10^5 and 10^2 s $^{-1}$ for temperatures in the range -50 to $+50^\circ C$. Similar conclusions have been drawn from experiments with octaethyl-porphyrin⁹⁷ (III) (figure 9.1).

With this activity in biochemical n.m.r. there would clearly be marked interest in any results that could be obtained from the present model system.

9.2.1 Results and Discussion

The ^{15}N n.m.r. peak in neat pyridine was observed as a triplet at 294.8 p.p.m. downfield from $^{15}NH_4^+$. The triplet splitting was 11.0 Hz. The coupling constant $^2J_{NH}$ has been reported^{94,95}, from the p.m.r. spectrum, to be in the region of -10.7 Hz.

^{15}N spectra of pyridinium fluoroborate dissolved in acetonitrile, without and with the addition of a large quantity of trifluoromethane sulphonic acid have been run without the observation of any intelligible peaks.

Whilst the results for neat base are in agreement with previously published data the failure to observe satisfactory spectra of the cation requires some comment. In the past, several reasons have been propounded for the nulling of ^{15}N resonances. Three are (i) the negative nuclear Overhauser effect (n.O.e.) which can only contribute under conditions of proton decoupling⁹⁸, (ii) exchange of the labile proton which can null the signal over quite a wide range of pH values⁹⁹ and (iii) inconvenient molecular correlation times¹⁰⁰.

Clearly the n.O.e. explanation is not relevant here since no decoupling has been used. Because no signal has been observed under several different conditions of pH the exchange rate must have been varied sufficiently for a signal to be observed for at least one solution. The third explanation seems to be the most reasonable. If molecular tumbling in solution is slow then under the conditions of Fourier Transform n.m.r., lines become very broad and possibly undetectable, even when, as in the present case, over 8000 scans have been accumulated.

9.3 ^1H n.m.r. studies

Proton magnetic resonance studies of ^{15}N -pyridine have been reported with the ^{15}N results discussed in the previous section^{94,95}. No mention has however been made

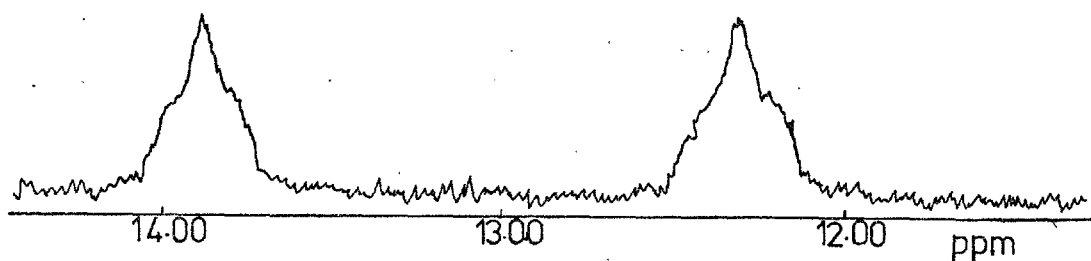
of the N-H proton resonance in the pyridinium ion. Under the conditions used by Lichter and Roberts⁹⁵ (pyHCl in methanol) exchange is too fast for any results of interest to be observed. Price⁹⁴ however used pyridine dissolved in trifluoroacetic acid, conditions which would, in the light of experiments^{45,53} with ^{14}N pyridine be expected to slow the exchange process sufficiently for splitting of the N-H proton peak to be observed. No results for the other protons are reported in this section.

9.3.1 Results and Discussion

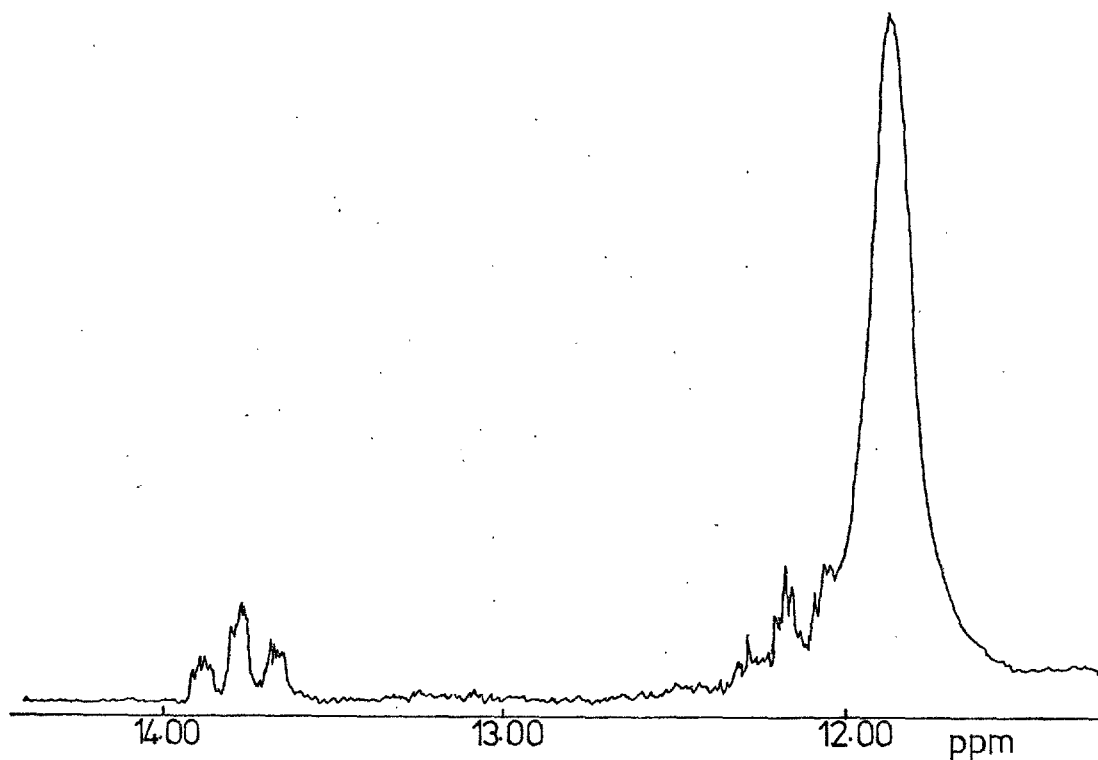
Each sample submitted for ^{15}N n.m.r. spectroscopy was examined by p.m.r. first. The two spectra in figure 9.2 illustrate the effect of reducing the pH of the sample using trifluoromethane sulphonic acid. In each case the pyridinium ion concentration was 1.5 M in acetonitrile. At pH = 1.7 each peak of the doublet due to coupling with the ^{15}N nucleus ($^1J_{\text{NH}} = 95 \text{ Hz}$) shows an incipient triplet. At pH = -0.2 the triplets can be clearly seen ($^2J = 6 \text{ Hz}$). The large peak at 11.87 ppm is that of the acid proton of trifluoromethane sulphonic acid. These triplets are the result of coupling between the N-H and α protons. Clearly exchange is sufficiently slow for these effects to be observed.

9.4 The Raman Spectrum of ^{15}N pyridine, 1700-500 cm^{-1}

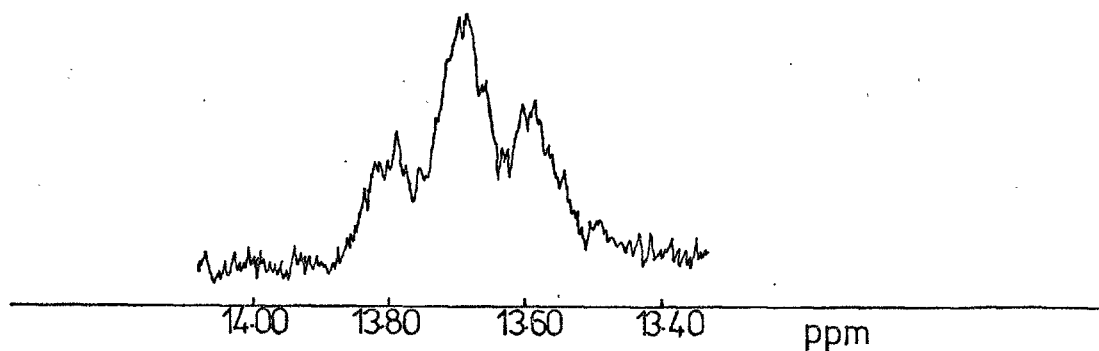
The spectrum is shown in figure 9.3 with that of natural abundance ^{14}N pyridine for comparison. The bands are listed in table 9.1. The assignment follows that of Corrsin, Fax and Lord⁷³ as amended by Green, Kynaston and Paisley⁷⁰.



A : pH = 1.7



B : pH = -0.2, the peak at $\delta = 11.87$ ppm is due to excess acid.



C : enlargement of B

Figure 9.2 : The N-H proton resonance of $\text{pyH}^+\text{BF}_4^-$ in CH_3CN , with added $\text{CF}_3\text{SO}_3\text{H}$.

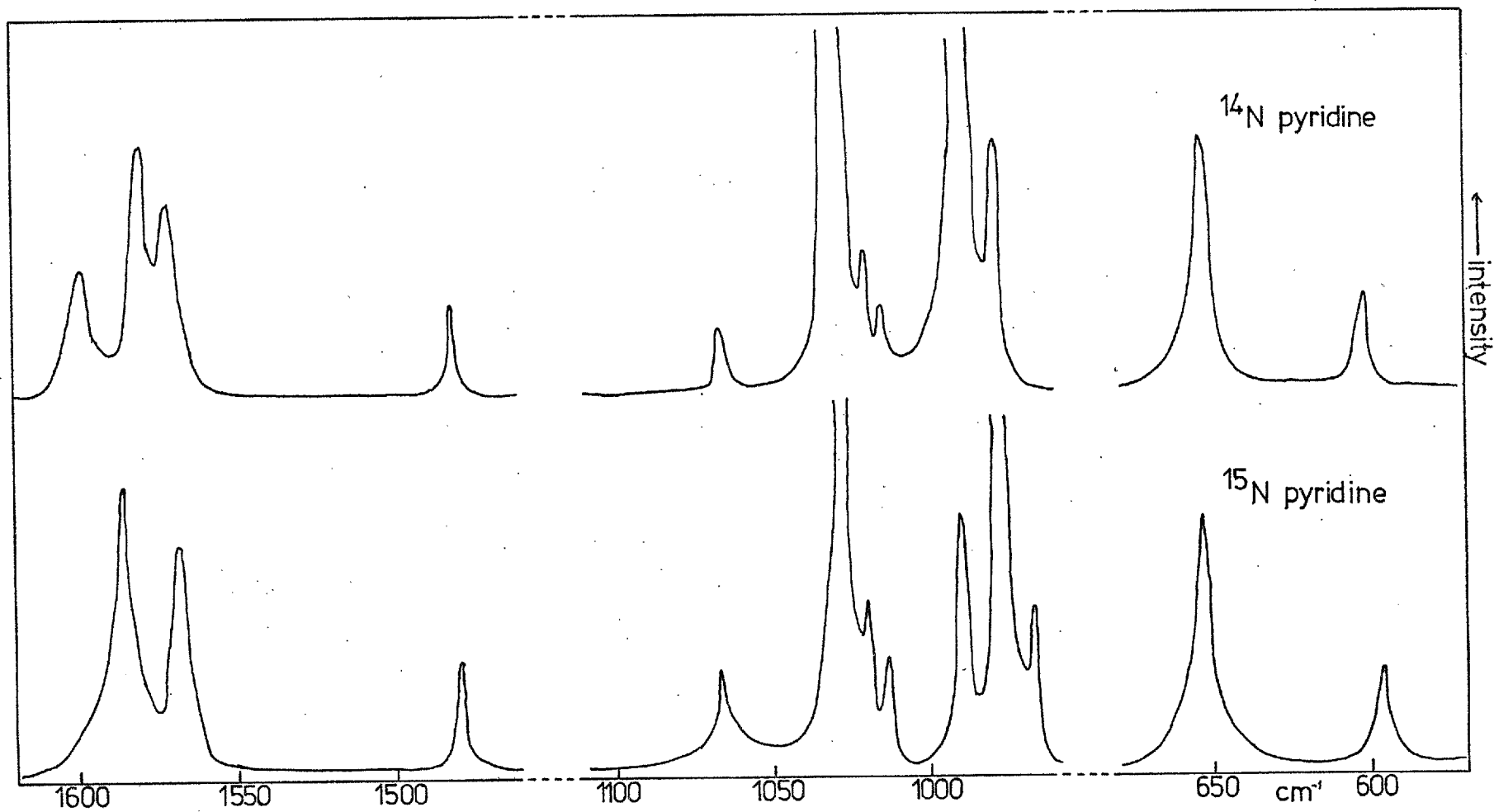


Figure 9.3 : The Raman spectra of ^{14}N and ^{15}N pyridine.

TABLE 9.1

The Raman spectra of ^{14}N and ^{15}N pyridine.

Assignment	^{14}N -pyridine	^{15}N -pyridine
	1597 m	
ν_{8a}	1580 s	1587 s
ν_{8b}	1572 m	1568 s
ν_{19a}	1482 w	1480 m
ν_{18a}	1068 w	1067 m
ν_{12}	1030 vs	1029 vs
	1020 w	1020 w
	1015 w	1014 w
		990 s
ν_1	990 vs	977 vs
ν_{17a}	979 s	
		967 w
ν_{6b}	653 s	652 s
ν_{6a}	602 m	596 m

At present two normal co-ordinate treatments of the pyridine molecule exist: those of Wilmshurst and Bernstein¹⁰¹ and of Long, Murfin and Thomas⁹⁰.

Both are apparently valid with the present knowledge of the infra-red spectra, however it is possible that vibrational data of ^{15}N enriched samples might be of assistance in confirming the validity of one model over the other.

Further comments upon the spectra are not possible without a more detailed examination of the system, however the data is presented here in the hope that it might be of some use to other workers.

CHAPTER 1010. CONCLUSION10.1 Spectroscopic and kinetic models

At the outset the intention of this work was to measure a proton transfer rate within a formally symmetric hydrogen bonded complex. Various spectroscopic methods were used and failed to provide a means of measuring the rate of prototropism. In the case of fluorescence it appears that time resolved methods might be more appropriate. The fluctuation proposals imply that no tunnelling mode, ν_T , should be observed in the infra-red because prototropism occurs by the lowering of the barrier. Additionally in view of the pseudo-static asymmetry of the potential, environmental fluctuations may lead to proton transfer as the field turns through 180° . Reasons have also been given for the inability of p.m.r. to provide proton transfer rates.

It is interesting to compare the spectroscopic and kinetic approaches to proton transfer reactions and hydrogen bonding. Whilst for the spectroscopist the life-time of the hydrogen bond is longer than the characteristic measuring time and the bond can therefore be considered a semi-permanent phenomenon, the kineticist sees it merely as one brief intermediate in his reaction scheme during which prototropism occurs. Perhaps the most striking evidence of these different approaches is the type of potential function that is drawn along the reaction coordinate (figure 10.1).

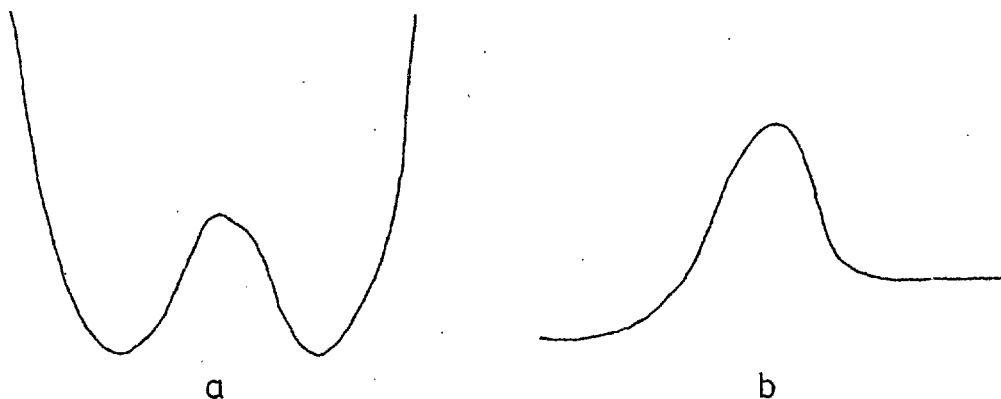


Figure 10.1 : Generalised reaction coordinates.

The spectroscopist knows the complex to have a finite life-time and therefore shows the function as two wells (10.1.a). The kineticist on the other hand sees the reactants approach and the products leave with a barrier in the middle at the closest point of approach (10.1.b). As a result the treatments of proton tunnelling are entirely different - between quantised states in spectroscopy and between continua in kinetics.

There is clearly a need for a unification of these two theories. A generalised potential along the reaction coordinate is shown in figure 10.2.

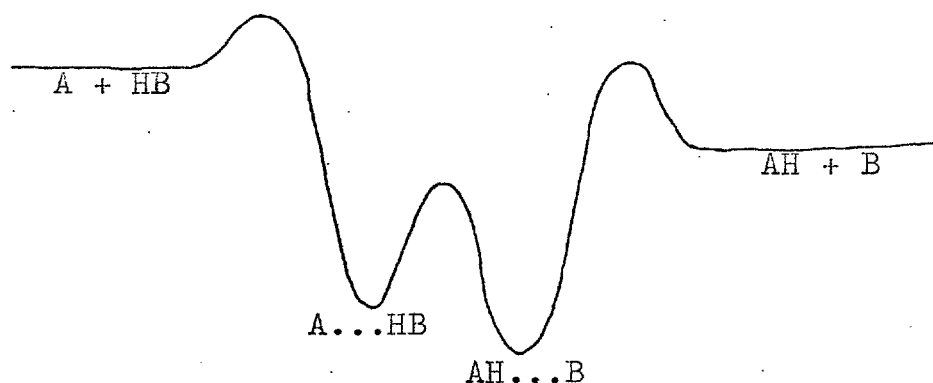


Figure 10.2 : A unified reaction coordinate.

It is evident that in a comprehensive model consideration must be given to bending and stretching of the hydrogen

bonded complex. Vibrational quantisation in the complex is likely but as shown in chapter seven the levels will be blurred. Proton tunnelling is then possible, but more important if transfer is predominantly through the ground state. It is suggested that an approach along these lines would be valuable.

10.2 Internal mode frequencies versus ΔpK_a

Dean and Wood¹² have given evidence that inter-comparison between various asymmetric complexes can be made upon the basis of ΔpK_a , the pK_a difference between the proton donor and proton acceptor. In this section internal mode data for pyridine hydrogen bonded to a variety of different bases are presented and discussed. The basis of the discussion is whether the single frequency associated with each mode in the symmetric complex $(py_2H)^+$ is characteristic of pyridine in its donor or acceptor rôle. Low temperature results from chapter four suggest that it is the proton donor moiety which gives rise to these bands at room temperature. There is a second method which might be able to answer this dichotomy and it arises from the work of chapter five. Various complexes of formula $(pyHB)^+$ have been examined, in which B is either a stronger or a weaker base than pyridine. It is possible that the progression of internal mode frequencies from the system in which $|\Delta pK_a|$ is large to the symmetric complex $(py_2H)^+$ could give the answer.

Two problems arise immediately. Firstly the symmetric complex with its highly polarizable hydrogen

bond may not fit very neatly into the trend and secondly if it does so, the trend may pass so smoothly through the symmetry complex that the origin of the band may not be at all clear. In addition the proposal assumes that the frequencies are not dependent upon the mass of the non-pyridine moiety. Figures plotted by Dean and Wood¹² suggest that a comparison with ΔpK_a is sufficient. Frequencies of selected internal pyridine modes are given in table 10.1. The base strength of the second moiety increases from left to right consequently pyridine is in the proton donor role to the left of the table and in the acceptor role to the right.

There seem to be very few trends in table 10.1, even amongst complexes in which the pyridine role is the same. What we might hope to find would be a discontinuity in a trend at the symmetric complex such that it is clear on which side of the discontinuity the $(py_2H)^+$ frequency lies. This is evidently not the case for any of these modes. Indeed the lack of trends makes it unlikely that further pursuit of this approach would be profitable.

TABLE 10.1. Internal mode frequencies (in cm^{-1}) of the pyridine moiety in various asymmetric complexes, $(\text{pyHB})^+$

B	CH_3CN^*	Cl^-	tz	3-Brpy	py	4 mepy	meim	Et_3N	MeO^- or OH^-	neat pyridine
$\text{pK}_a(\text{B})$	-	-	2.55		5.17	6.02	6.95			
ν_{8a}	1640	1630	1636	1637	1639	1645				1583
ν_{8b}	1612	1605		1613	1603			1596	1595	1572
ν_{19a}	1542	1532	1545	1540	1549		1550		1487	1482
ν_{19b}	1490	1485	1488	1489	1493	1490	1488		1443	1439
ν_{9a}	1207	1200	1205	1201	1205	1208	1205	1216	1215	1218
ν_{15}	1174	1165	1165		1167	1175		1148	1150	1148
ν_{18a}	1050	1058			1040	1035	1038		1068	1068
ν_1	997	1003			1007	1004	1007	1002	1001	993
ν_{11}	675	685	681	679	684	687	686		709	703
ν_{6a}	610	607	621		628	627	623	618	617	605
REF.	69	69	12	-	69	102	12	103	8	69

* "free salt"

tz = thiazole

meim = N-methylimidazole

10.3 Fluctuation model

Since the writing of chapter seven, attention has been drawn to the work of Efimov and Naberukhin¹⁰⁴. They have used a fluctuation model to reproduce band shapes for the OH stretching modes in various hydrogen bonding complexes involving water. A statistical distribution of complex molecules caused by local differences in the environment gives rise to band-broadening. Apart from the extensive mathematical treatment employed by Efimov and Naberukhin, their approach broadly differs from that described in chapter seven in that the present method covers only one symmetrical complex unit in which the N-N distance fluctuates and the proton transfer rate is consequently enhanced.

10.4 Conclusions

The work described in this thesis takes the study of the symmetric hydrogen bonded complexes a stage further. In particular the origin of the internal mode frequencies observed at room temperature in the proton donor moiety has been established. It would be of value to examine the entire internal mode region under excess donor conditions since no satisfactory evidence exists to show that acceptor mode frequencies are not observed except in the case of the ring elongation mode, ν_{6a} .

It seems that the kind of gross examination of the infra-red spectra of complex cations carried out here and in previous work is not sufficient to provide a basis for the complex calculations that now seem necessary^{82,104}.

Theoretical studies of isolated complex units are of little value when it is clear that experimental conditions play so important a part in moulding the complex proton potential.

Both p.m.r. and electronic spectral techniques could be used more extensively in the examination of symmetric complexes. Suggestions for their further use have been given in the appropriate chapters. In particular p.m.r. as a technique in which concentration restraints do not apply (unlike U.V. absorbance and fluorescence) has advantages which should be utilised.

CHAPTER 11.11. EXPERIMENTAL TECHNIQUES11.1 Preparation of Compounds

In general, bases (Hopkin and Williams, B.D.H., Aldrich or Ralph Emanuel) were purified by twice distilling them from potassium hydroxide. Halogenated pyridines were distilled from vacuum dried molecular sieve 4A twice. All bases were stored over molecular sieve (dried in a vacuum oven at 120°C overnight) in a dry box (drying agent phosphorus pentoxide) under nitrogen.

Salts were prepared from three acids: perchloric, fluoroboric and hexafluorophosphoric (Analar, B.D.H. and Alfa Products). In each case ice-cold acid was added drop-wise to an equimolar quantity of base with cooling. The fluorophosphate was prepared in a polypropylene beaker since the acid attacks glass. Evaporation of water on the vacuum line gave a white precipitate which was recrystallised twice from methanol. Salts were dried thoroughly on the vacuum line with gentle warming. Care was taken with dry perchlorates because of their well-known instability.

Acetonitrile (B.D.H. spectroscopic grade) was not distilled but stored over molecular sieve in a dry box.

¹⁵N pyridine (Prochem) was received in a sealed n.m.r. tube and spectra were run without breaking the tube. ¹⁵N pyridinium fluoroborate was prepared on a microscale in the same way as other salts. Trifluoromethane sulphonic acid (Aldrich) was used without further

treatment. Care was taken only to open the bottle in the dry box.

3,5 dimethylpyridine symmetric complexes were prepared by dissolving the salt in hot base. The complex crystallised out on cooling the solution. In some cases the complex was recrystallised from methanol or acetonitrile. Crystals were washed with toluene and dried overnight on the vacuum line. Samples for crystallographic examination were recrystallised from base and not treated any further.

Purity of compounds (in particular freedom from water) was checked by elemental analysis and infra-red and n.m.r. spectroscopy.

All salts were deuterated by three or four recrystallisations from D_2O (Merck Sharpe and Dohme). Handling of the compounds was carried out as far as was possible under a nitrogen atmosphere. Deuteration was checked by infra-red spectroscopy.

Deuterated 3,5 dimethylpyridine complex crystals were prepared from deuterated salt in the normal way.

11.2 Preparation of Samples for Spectroscopy

All preparation of samples was carried out in dry boxes (using phosphorus pentoxide drying agent) under nitrogen. Samples for which an accurate knowledge of concentration was required were weighed outside the dry box but care was taken to restrict the exposure to the atmosphere. For liquid samples syringes of appropriate sizes were used to measure volume. In calculating

concentrations no allowance was made for the volume of the solute.

In the n.m.r. experiments, reported in chapter 2, where a progressively increasing base concentration was required successive quantities of base were added to the solution containing a fixed quantity of salt. Concentration calculations were based upon the estimated volume of the solution at the mid-point of the run.

11.3 Spectroscopy

Infra-red spectra in the $4000-400\text{ cm}^{-1}$ range were obtained upon a Perkin-Elmer 325 instrument, in both transmittance and absorbance modes. Spectra were run of pure liquids, of solutions and of solids in mull (nujol or hexachlorobutadiene) form between sodium or silver chloride plates. Pathlengths were generally 50 or $100\text{ }\mu$. Potassium bromide discs of solid samples were also used.

Low temperature infra-red spectra, in the range $1700-400\text{ cm}^{-1}$, were run using an R.I.I.C. variable temperature cell, cooled with liquid nitrogen. The sample, in solution between AgCl plates, was cooled rapidly by plunging the cell, in the cell-holder, into a flask of liquid nitrogen. The assembly was then rapidly transferred to the outer jacket (KBr windows) and the space between evacuated. The temperature was maintained by periodically topping-up the central vessel with liquid nitrogen. No heating, save of the outer windows in order to prevent condensation, was applied to the cell. The temperature was estimated, using a Eurotherm PID/SCR temperature controller with a chromel-alumel junction,

to be about -180°C . Pathlengths for the low temperature experiments were 50μ .

Raman spectra were obtained with a Spex Ramalog 5 triple monochromator system having a photon counting detector. The spectra were obtained by excitation with the 530.9 nm line from a Coherent Radiation Model 52K Krypton Ion Laser. The powers at the sample were in the range 100-150 mW.

^1H nuclear magnetic resonance spectra were measured on Perkin Elmer R12 A and R12 B instruments, operating at 60 MHz. Single line chemical shift measurements were made by shifting the field by a known amount during the run, so that the line of interest and the reference line (tetramethylsilane) might appear closer together and the time of measurement might be shortened to reduce the error of a constantly drifting field. Each peak was measured twice - scanning both down- and up-field. The error in the measurements was estimated to be 0.02 p.p.m. The temperature of measurement was 34°C .

^{15}N n.m.r. measurements were carried out at 6.08 MHz using a Bruker WP60 F.T. instrument at the Open University, Milton Keynes. The sample, in a 5 mm o.d. n.m.r. tube, was concentrically mounted in a Wilmad 15 mm o.d. tube using teflon rings. ^1H n.m.r. and Raman spectra were also run in the 5 mm tube.

Ultra-violet and fluorescence spectra were obtained on Perkin Elmer 402 and 204 instruments respectively.

APPENDIX 1.

The Evaluation of the three parameters, K_c , δ_{BH} and δ_{BHB} , from the p.m.r. results using the computer program DARWIN.

In each experimental run carried out, the total concentration of proton donor was kept constant and the variation of observed chemical shift of the N-H proton resonance with total proton acceptor concentration was monitored. The program DARWIN evaluates the parameters K_c , δ_{BH} and δ_{BHB} by fitting a calculated curve to the experimental points.

The program requires that the user selects initial values for the three parameters and the step-sizes initially required between the test points. In the first cycle of the program, 125 combinations of values of the three parameters are used in a 5 x 5 x 5 array, with the initially chosen values at the centre and the other points at ± 1 and ± 2 step-sizes. For each combination the program calculates the expected values of the chemical shift for each proton acceptor concentration using equations 2.6, 2.8 and 2.9 of section 2.7. The combination which gives the smallest value to the sum of the squares of the deviations is used as the centre of the next cycle. The step-sizes are reduced in any dimension for which the result is not at ± 2 step-sizes.

The program continues to run cycles of 125 combinations until either all the step-sizes are reduced to

predetermined values, or a selected number of cycles have been completed.

The resulting three parameters are used to calculate the chemical shifts at each value of [B] and these are printed out. Finally the standard deviations of the three parameters are calculated using the method of Marquardt¹⁰⁵. Routine FO1AAF is a standard program for matrix inversion from the Numerical Algorithm Group (NAG) library. The program contains a number of fail-safe devices to indicate where the error is occurring and to allow a continuation to the next data set.

Because of the limited space available the program in the following pages is given with a field width of 56 spaces instead of the usual 72.

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PROGRAM DARWIN (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=
+OUTPUT)

  DIMENSION CB(20),DOB(20),CC(20),DEV(20),TITLE(10),
+A(20,3),S1(20,3),AT(3,20),S2(3,3),S3(3,3),DE(20),
+Z(1),Z1(3)

1  N=0

  IMIN=0

  JMIN=0

  KMIN=0

  I1=0

  I2=0

  DAS=0.16

C DATA TO BE READ IN. FIRST CARD CONTAINS (1) ESTIMATED
C EQUILIBRIUM CONSTANT AND FIRST STEP SIZE, (2) ESTI-
C MATED CHEMICAL SHIFT OF COMPLEX AND FIRST STEP SIZE,
C (3) CONSTANT INITIAL SALT CONCENTRATION, (4) CHEMICAL
C SHIFT OF FREE SALT (EXPERIMENTAL OR ESTIMATED). FORMAT
C HAS SIX LOCATIONS, EACH WITH DECIMAL POINT IN COLUMN
C (10N+6). THE INITIAL BASE CONCENTRATION AND CORRESPOND-
C ING CHEMICAL SHIFT AT EACH POINT APPEAR ON SUBSEQUENT
C CARDS. THE LAST CARD IN EACH RUN CONTAINS 88. AND THE
C LAST CARD IN THE LAST RUN HAS 99. IN PLACE OF CB(N).

  READ(5,1001) (TITLE(IT),IT=1,10)

1001 FORMAT(10A8)

  READ(5,1002) ECM,ECS,DCM,DCS,CA,DAM

1002 FORMAT(6F10.4)

  WRITE(6,1003)

1003 FORMAT(/// 15X, '*****'///)

  WRITE(6,1004) (TITLE(IT),IT=1,10)

1004 FORMAT(20X,10A8)

```

```

WRITE(6,1005) ECM,ECS
1005 FORMAT(///20X,'FIRST GUESS AT EQUILIBRIUM CONSTANT
+ =' ,F10.4,/20X,'FIRST STEP SIZE FOR EQUILIBRIUM CO
+NSTANT =' ,F10.4)
WRITE(6,1006)DCM,DCS
1006 FORMAT(///20X,'FIRST GUESS AT CHEMICAL SHIFT OF CO
+MPLEX =' ,F10.4,/20X,'FIRST STEP SIZE FOR CHEMICAL
+SHIFT OF COMPLEX =' ,F10.4)
WRITE(6,1007) CA,DAM
1007 FORMAT(///20X,'CONCENTRATION OF SALT THROUGHOUT RU
+N =' ,F10.4,/20X,'FIRST GUESS AT CHEMICAL SHIFT OF
+FREE SALT =' ,F10.4,///)
2 N=N+1
READ(5,1008) CB(N),DOB(N),DER(N)
1008 FORMAT(F6.3,1X,F5.3,F3.2)
WRITE(6,1009) N,CB(N),N,DOB(N),DER(N)
1009 FORMAT(20X,'CB(' ,I2,' ) =' ,F6.3,5X,'DOB(' ,I2,' ) =' ,
+F6.3,5X,F5.3)
IF(CB(N).LT.80.) GO TO 2
IF(CB(N).GT.98.) I1=1
NR=N-1
I3=-1
C THE FOLLOWING SECTION PERFORMS THE LEAST SQUARES FITTING
C TO OBTAIN THE BEST VALUES OF THE EQUILIBRIUM CONSTANT
C AND CHEMICAL SHIFTS OF THE FREE SALT AND H-BONDED PROTON
C THE ROUTINE FAILS IF THE BEST VALUES CANNOT BE FOUND IN
C TEN CYCLES.
3 BIN=-1.0
IF(I3.GT.9.AND.IABS(IMIN).EQ.2) WRITE(6,1010)
1010 FORMAT(20X,'LIMIT DUE TO EQUILIBRIUM CONSTANT')

```

```

      IF(I3.GT.9.AND.IABS(JMIN).EQ.2) WRITE(6,1011)
1011  FORMAT(20X,'LIMIT DUE TO CHEM. SHIFT OF COMPLEX')
      IF(I3.GT.9.AND.IABS(KMIN).EQ.2) WRITE(6,1012)
1012  FORMAT(20X,'LIMIT DUE TO CHEM. SHIFT OF SALT')
      I3=I3+1
      DO 20 I=1,5
      EC=ECM+ECS*FLOAT(3-I)
      DO 20 J=1,5
      DC=DCM+DCS*FLOAT(3-J)
      DO 20 K=1,5
      DA=DAM+DAS*FLOAT(3-K)
      BI=0.0
      DO 10 N=1,NR
      GC=CA+CB(N)+1.0/EC
      DE=DA+(DC-DA)*(GC-SQRT(GC*GC-4.0*CA*CB(N)))*0.5/CA
      BI=(DE-DOB(N))**2+BI
10    CONTINUE
      IF(BIN.LT.0.0) BIN=BI
      IF(BI.GT.BIN) GO TO 20
      BIN=BI
      IMIN=3-I
      JMIN=3-J
      KMIN=3-K
20    CONTINUE
      ECM=ECS*FLOAT(IMIN)+ECM
      DCM=DCS*FLOAT(JMIN)+DCM
      DAM=DAS*FLOAT(KMIN)+DAM
      WRITE(6,1013) I3,ECS,DCS,DAS,ACM,DCM,DAM,BIN
1013  FORMAT(20X,I2,5X,3(F6.4,5X),5X,3(F7.4,5X),5X,F12.9)
      IF(IABS(IMIN).NE.2.AND.ECS.GT.0.02) ECS=ECS*0.25

```

```

IF(IABS(JMIN).NE.2.AND.DCS.GT.0.01) DCS=DCS*0.25
IF(IABS(KMIN).NE.2.AND.DAS.GT.0.01) DAS=DAS*0.25
IF(I3.GT.10) GO TO 6
IF(IABS(IMIN).EQ.2.OR.IABS(JMIN).EQ.2.OR.IABS(KMIN
+).EQ.2) GO TO 3
IF(I2.EQ.1) GO TO 4
I3=-1
IF(ECS.GT.0.01.OR.DCS.GT.0.01.OR.DAS.GT.0.01)GO TO 3
I2=1
GO TO 3

C THE BEST VALUES HAVE NOW BEEN OBTAINED. THE FOLLOWING
C SECTION EVALUATES THE CHEMICAL SHIFT AT EACH POINT
C USING THESE VALUES AND PRINTS THEM OUT.

4 BIN=SQRT(BIN/FLOAT(NR))
WRITE(6,1014) ECM,DCM,DAM,BIN
1014 FORMAT(20X,'EQUILIBRIUM CONSTANT = ',F6.3, //15X,
+'CHEMICAL SHIFT IN COMPLEX = ',F6.3, //18X,'CHEMIC
+AL SHIFT IN SALT = ',F6.3, //22X,'STANDARD DEVIATI
+ON = ',F6.3,///)
WRITE(6,1015)
1015 FORMAT(22X,'BASECONCO COMPLEX DELTAOBS DELTAEVAL')
DO 30 N=1,NR
GC=CA+CB(N)+1.0/ECM
CC(N)=(GC-SQRT(GC*GC-4.0*CA*CB(N)))*0.5
DEV(N)=(DCM-DAM)*CC(N)/CA+DAM
WRITE(6,1016) CB(N),CC(N),DOB(N),DEV(N)
1016 FORMAT(20X,4F10.4)
30 CONTINUE

C FINALLY THE STANDARD DEVIATIONS FOR THE THREE EVALUATED
C QUANTITIES ARE OBTAINED FROM THE COVARIANCE MATRIX

```

C WHICH IS DERIVED FROM THE JACOBIAN MATRIX ACCORDING
C TO THE METHOD OF MARQUARDT.

```

      DO 40 L=1,NR
      GC=CA+CB(N)+1.0/ECM
      GU=SQRT(GC*GC-4.0*CA*CB(N))
      A(L,1)=(DCM-DAM)*(GC/GU-1.0)/(2.0*CA*ECM*ECM)
      A(L,2)=1.0-(GC-GU)*0.5/CA
      A(L,3)=1.0-A(L,2)
40  CONTINUE
      DO 50 M=1,3
      DO 50 L=1,NR
      S1(L,M)=A(L,M)/(DE(L)*DE(L))
      AT(M,L)=A(L,M)
50  CONTINUE
      DO 60 MA=1,3
      DO 60 MB=1,3
      S2(MA,MB)=0.0
      DO 60 L=1,NR
      S2(MA,MB)=AT(MA,L)*S1(L,MB)+S2(MA,MB)
60  CONTINUE
      IFAIL=1
      CALL FO1AAF(S2,3,3,S3,3,Z1,IFAIL)
      IF(IFAIL.EQ.0) GO TO 5
      WRITE(6,1017)
1017 FORMAT(10X, 'PROGRAM FAILED AT MATRIX INVERSION')
      WRITE(6,1018) IFAIL
1018 FORMAT(10X, 'FAILURE NUMBER IS',I2)
      WRITE(6,1019)
1019 FORMAT(20X, 'MATRIX S2 = ',/)
      WRITE(6,1020) ((S2(I1,I2),I2=1,3),I1=1,3)

```

```
1020 FORMAT (3(20X,3(5X,F12.4)/))
      GO TO 7
      5 WRITE(6,1021)
1021 FORMAT(10X, 'COVARIANCE MATRIX FOR THE THREE UNKNO
      +WNS = ')
      WRITE(6,1022)((S3(I1,I2),I2=1,3),I1=1,3)
1022 FORMAT(3(20X,3(5X,F12.8)/))
      DO 70 M=1,3
      VAR=SQRT(S3(M,M))
      IF(M.EQ.1) WRITE(6,1023) VAR
1023 FORMAT(10X, 'STANDARD DEVIATION OF EQUILIBRIUM CON
      +STANT = ', F10.6)
      IF(M.EQ.2) WRITE(6,1024) VAR
1024 FORMAT(10X, 'STANDARD DEVIATION OF CHEM. SHIFT OF
      +SALT = ', F10.6)
      IF(M.EQ.3) WRITE(6,1025) VAR
1025 FORMAT(10X, 'STANDARD DEVIATION OF CHEM. SHIFT OF
      +COMPLEX = ', F10.6)
      70 CONTINUE
      IF(I1.NE.1) GO TO 1
      STOP
      6 WRITE(6,10030
      WRITE(6,1026)
1026 FORMAT(20X, 'RANGE ERROR - YOU HAVE EXCEEDED THE L
      +IMITS SET')
      WRITE(6,1016) ECM,DCM,DAM
      7 IF(I1.NE.1) GO TO 1
      STOP
      END
```

APPENDIX 2.

Low temperature infra-red spectra of the pyridine system.

Spectra have been run between 1700 and 575 cm^{-1} in the absorbance mode. The wavelength scales are 25 and 10 cm^{-1} per cm. above and below 1000 cm^{-1} respectively.

The six systems studied are:

1. $(\text{py}_2\text{H})^+\text{BF}_4^-$ in CH_3CN
2. $(\text{py}_2\text{H})^+\text{PF}_6^-$ in CH_3CN
3. $(\text{py}_2\text{H})^+\text{BF}_4^-$ in CD_3CN
4. $(\text{py}_2\text{H})^+\text{PF}_6^-$ in CD_3CN
5. $(\text{py}_2\text{D})^+\text{BF}_4^-$ in CD_3CN
6. $(\text{py}_2\text{D})^+\text{PF}_6^-$ in CD_3CN

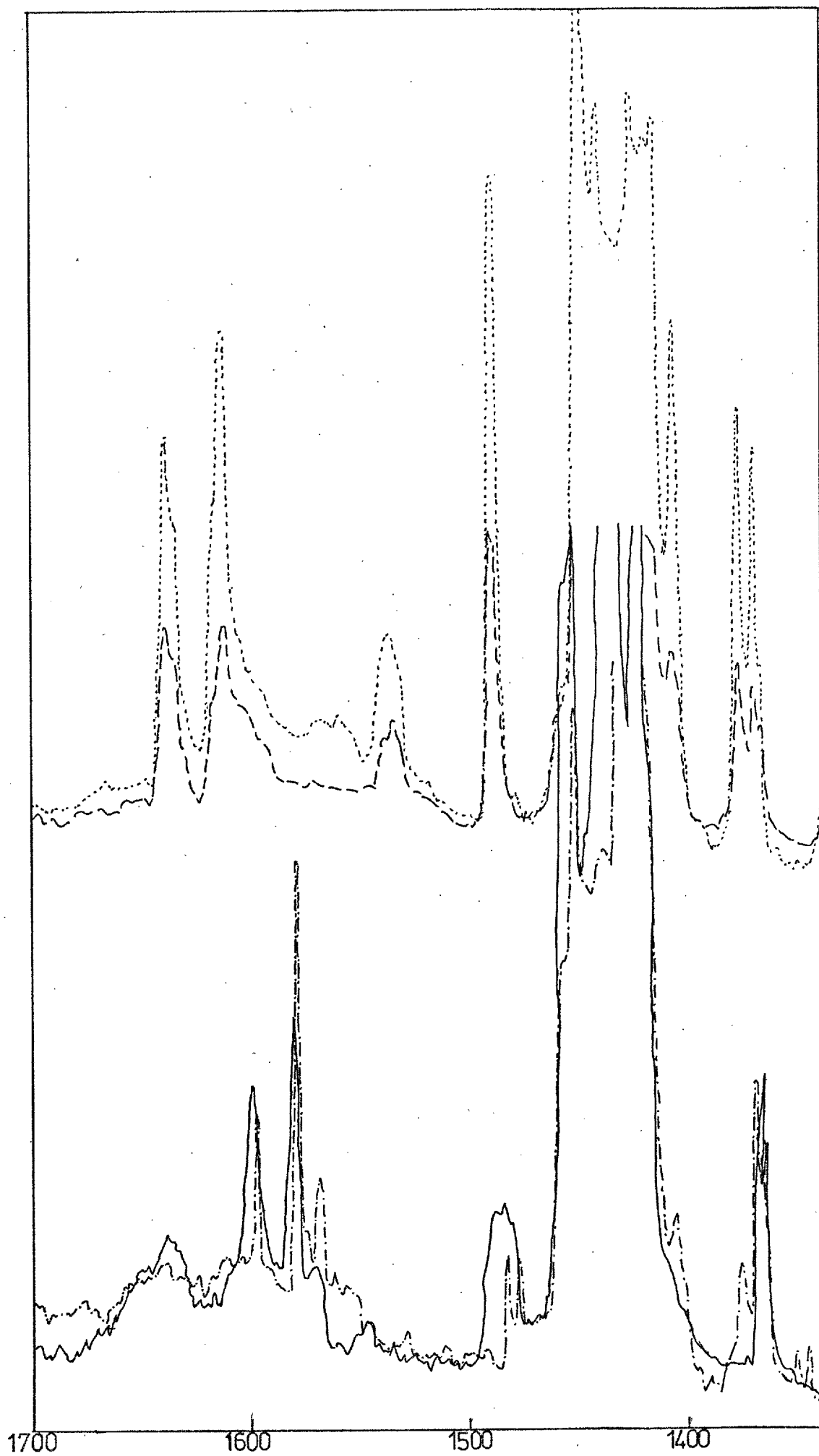
In this section each spectrum has been divided into five ranges whose divisions are approximately as follows:-

1. 1700 - 1340 cm^{-1}
2. 1360 - 1000 cm^{-1}
3. 1000 - 855 cm^{-1}
4. 860 - 715 cm^{-1}
5. 720 - 575 cm^{-1}

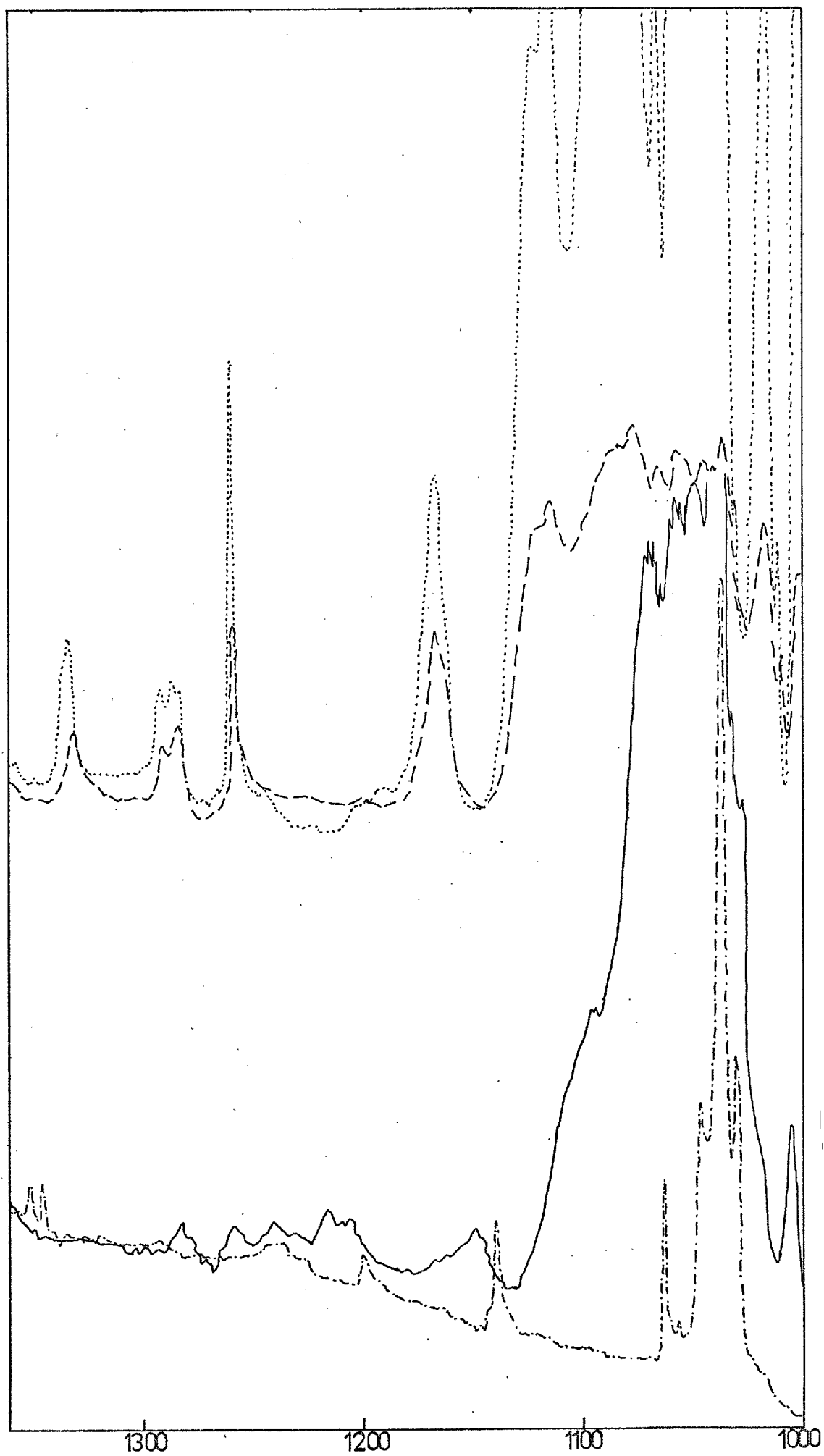
Each figure in this appendix is numbered according to the system and range, e.g. A2.3.4 refers to the 860-715 cm^{-1} range of the $(\text{py}_2\text{H})^+\text{BF}_4^-$ system in CD_3CN .

The individual spectra are distinguished, as in Chapter 4, by the notation:

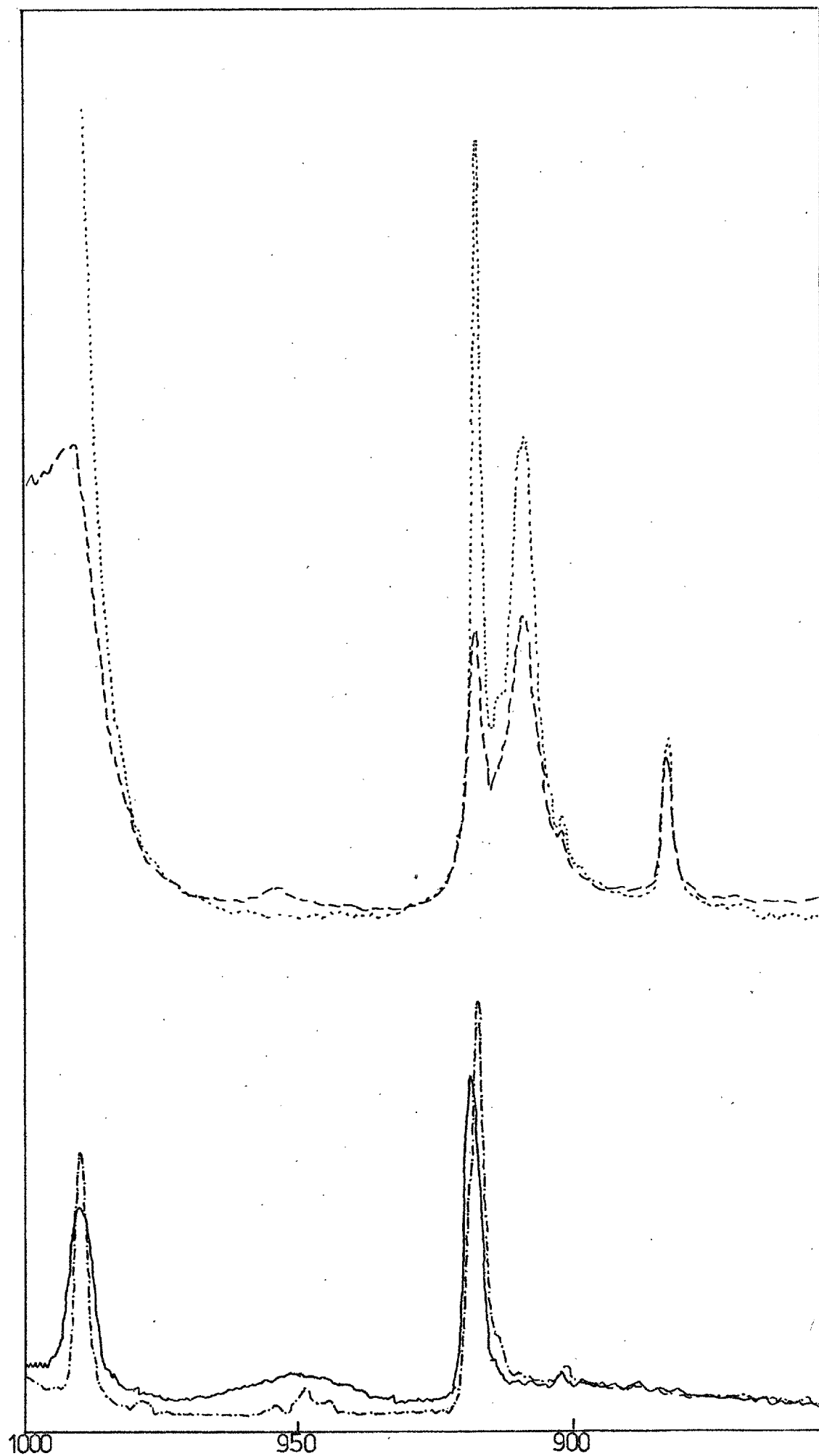
- . - . - . - .	1.0 M base
_____	{ 1.0 M base
	{ 0.25 M salt
.....	1.0 M salt
- . - . - . - .	{ 1.0 M salt
	{ 0.25 M base



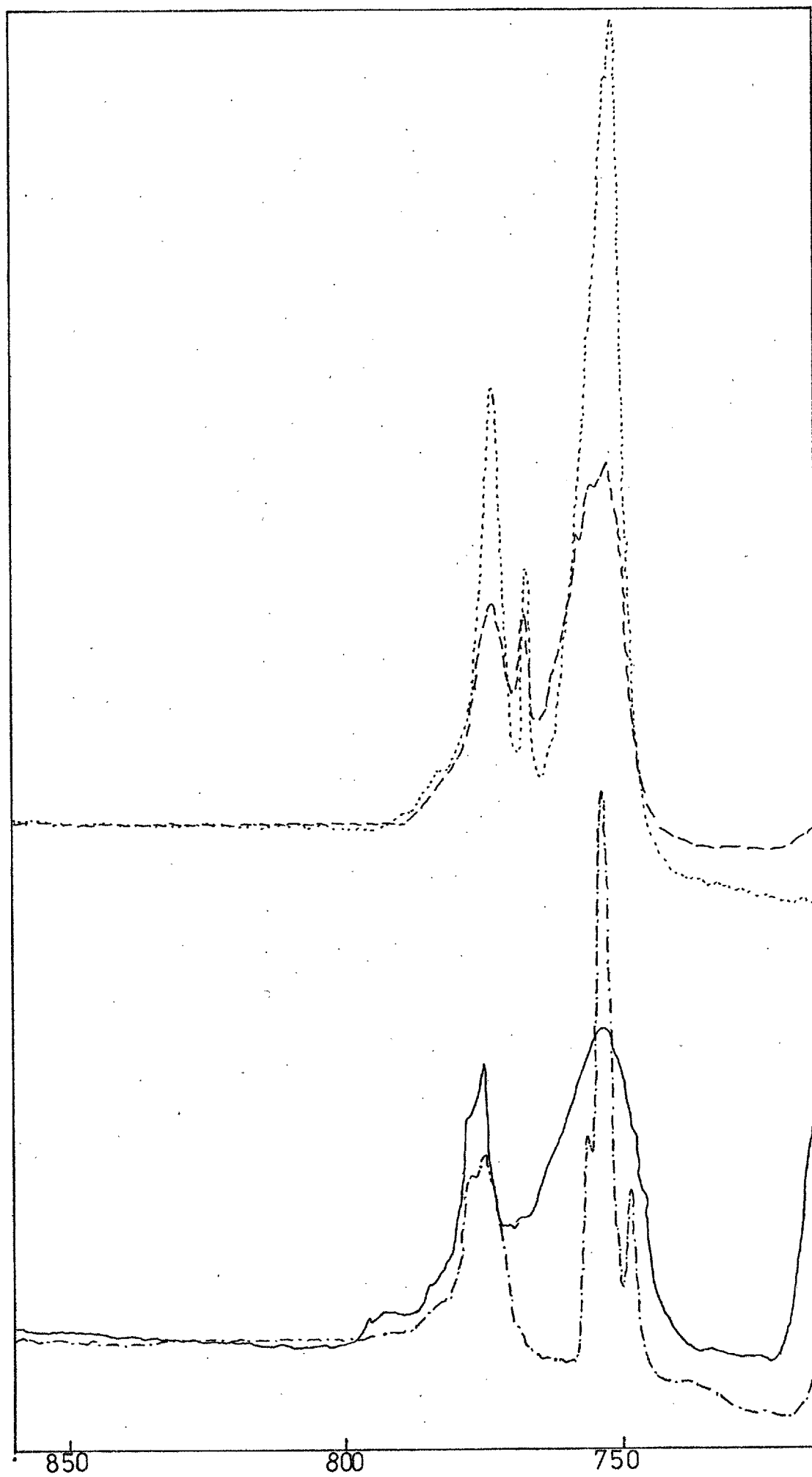
A2.1.2



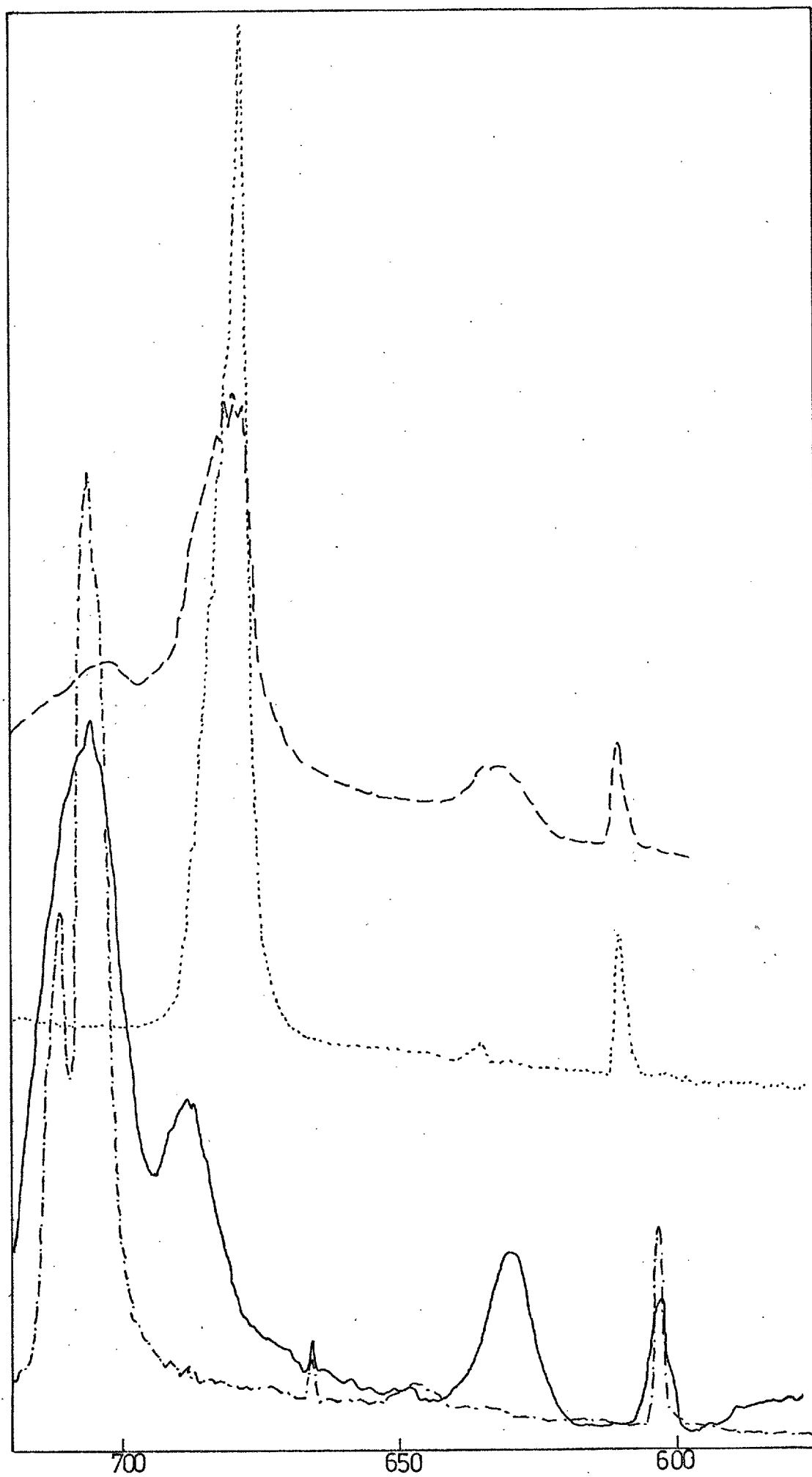
A2.1.3



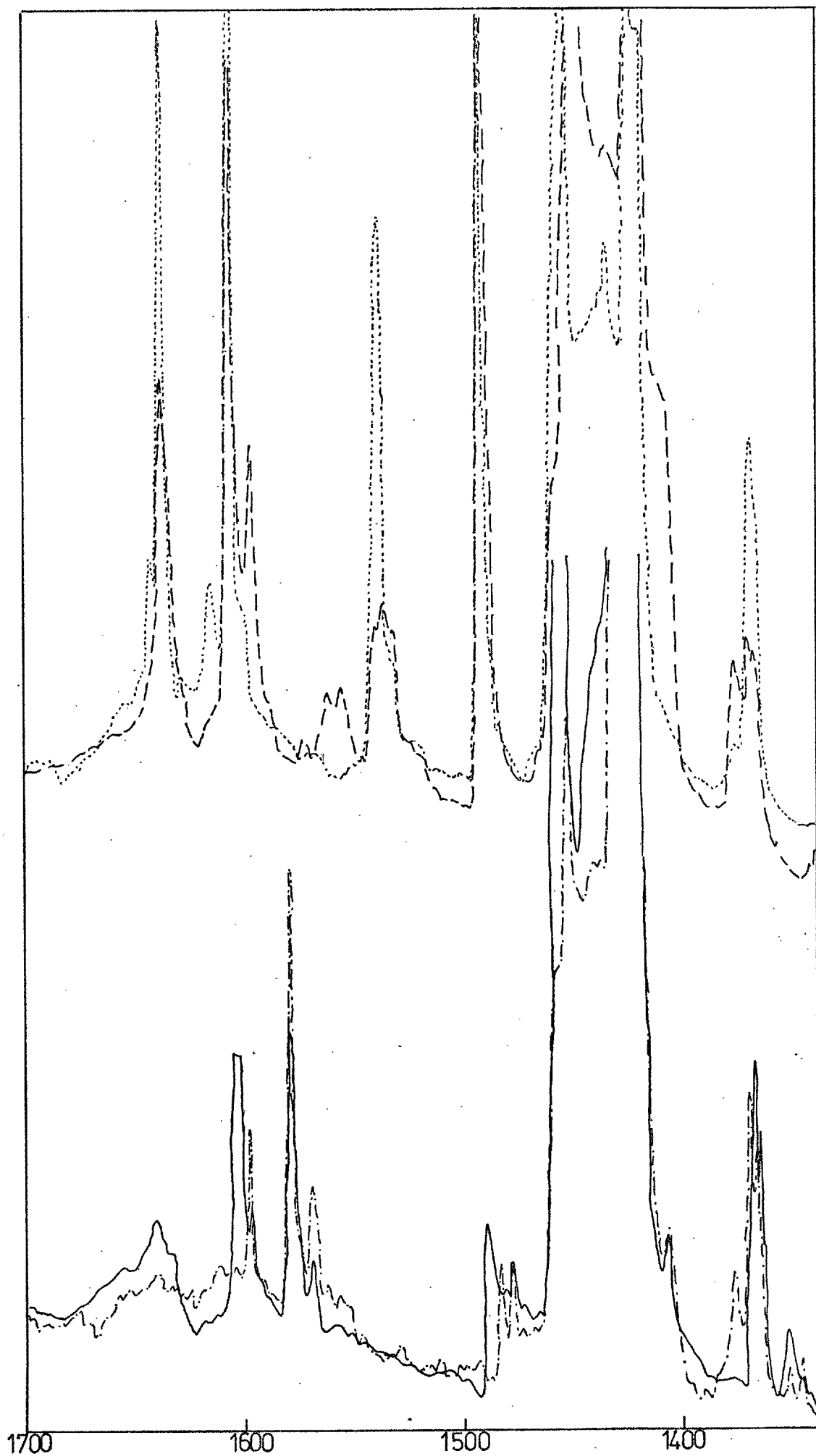
A2.1.4



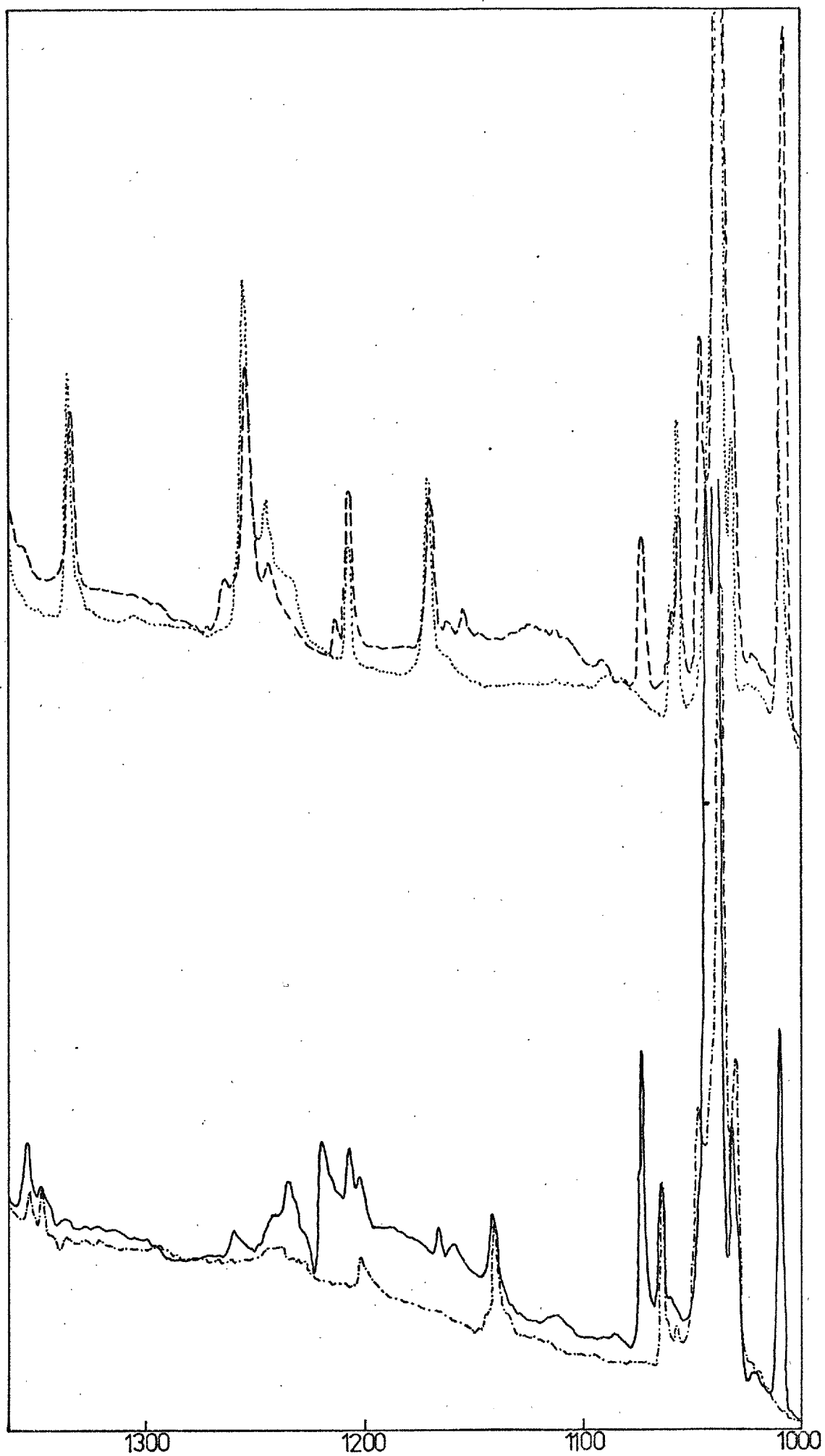
A2.1.5



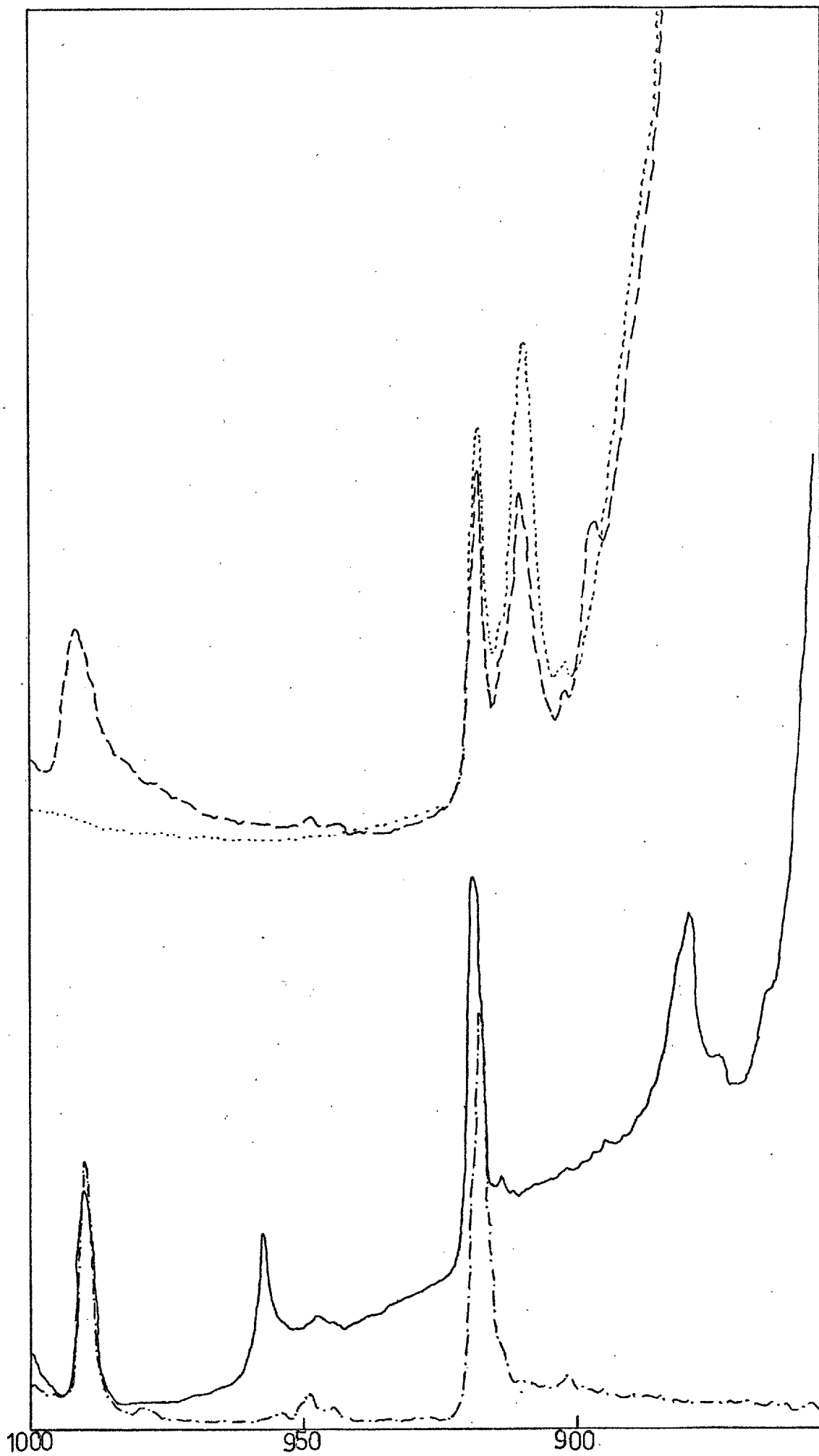
A2.2.1



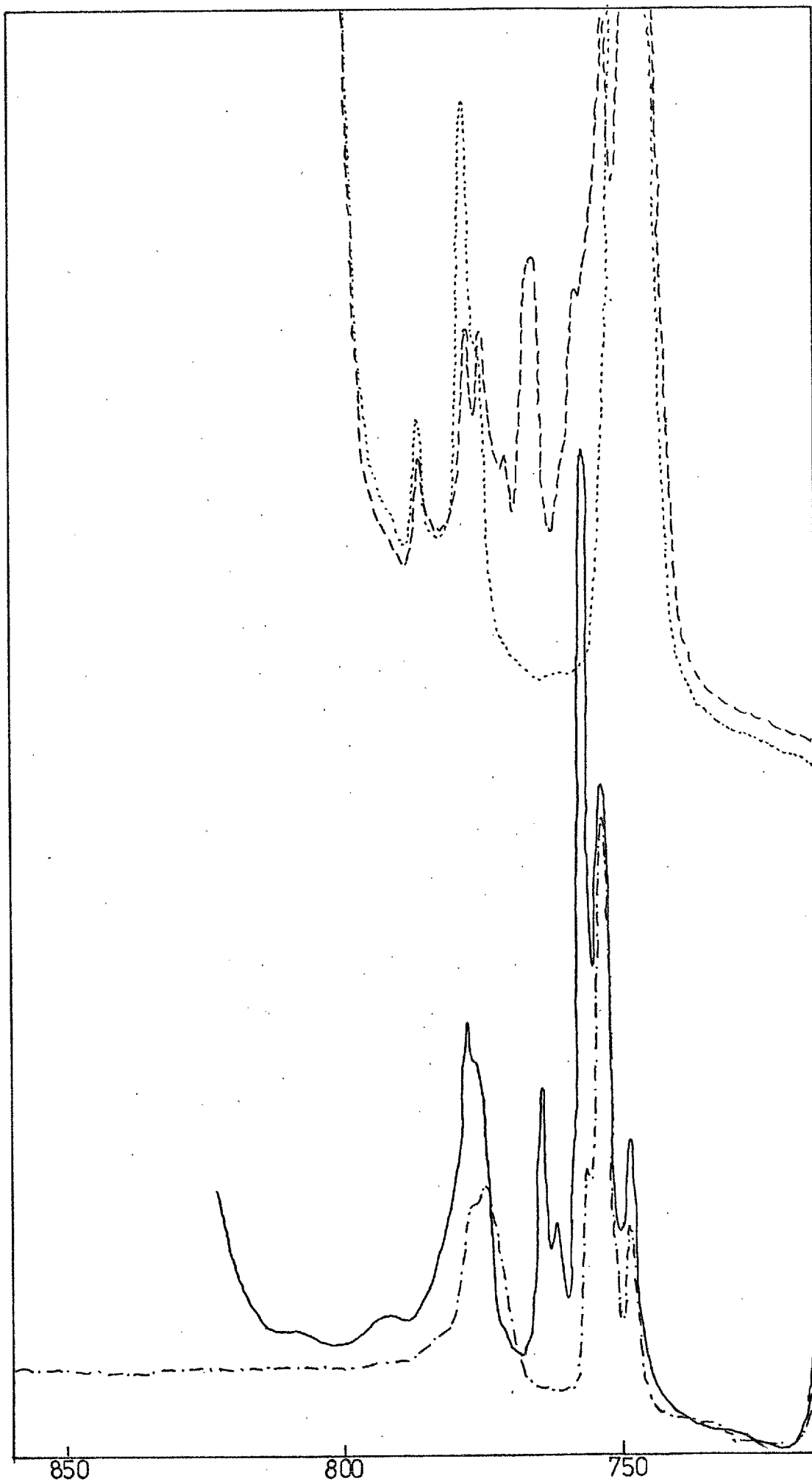
A2.2.2



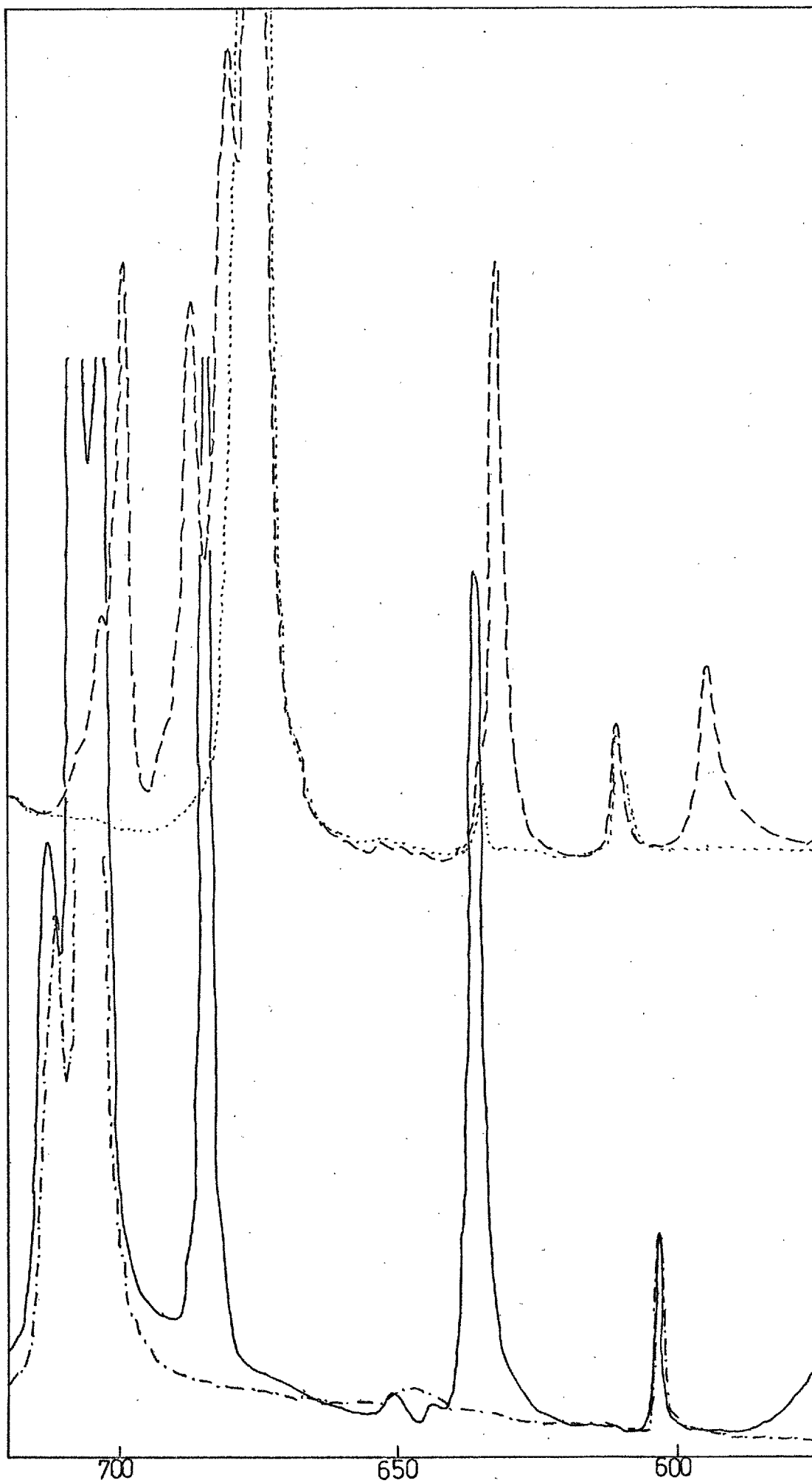
A2.2.3



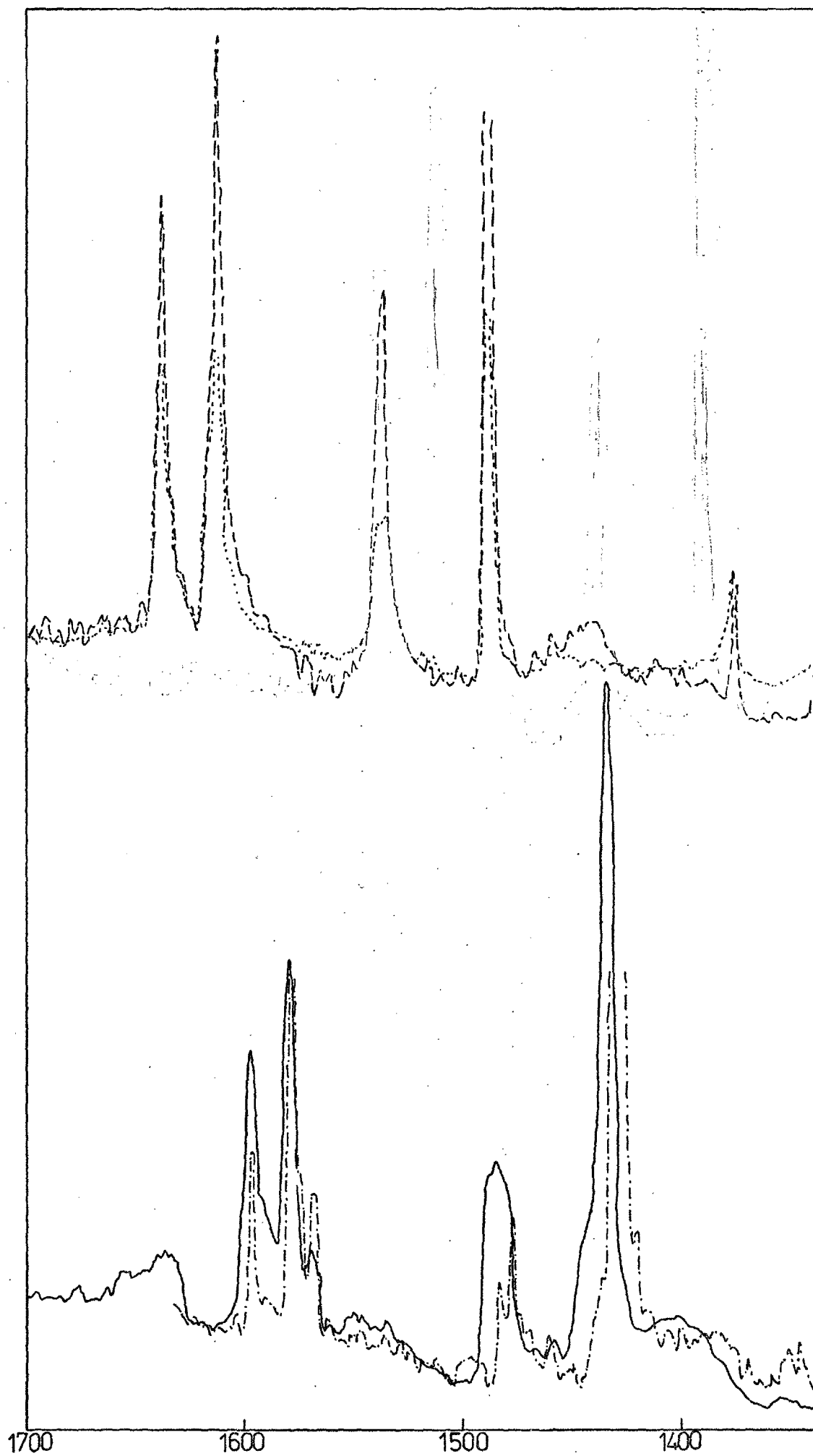
A2.2.4



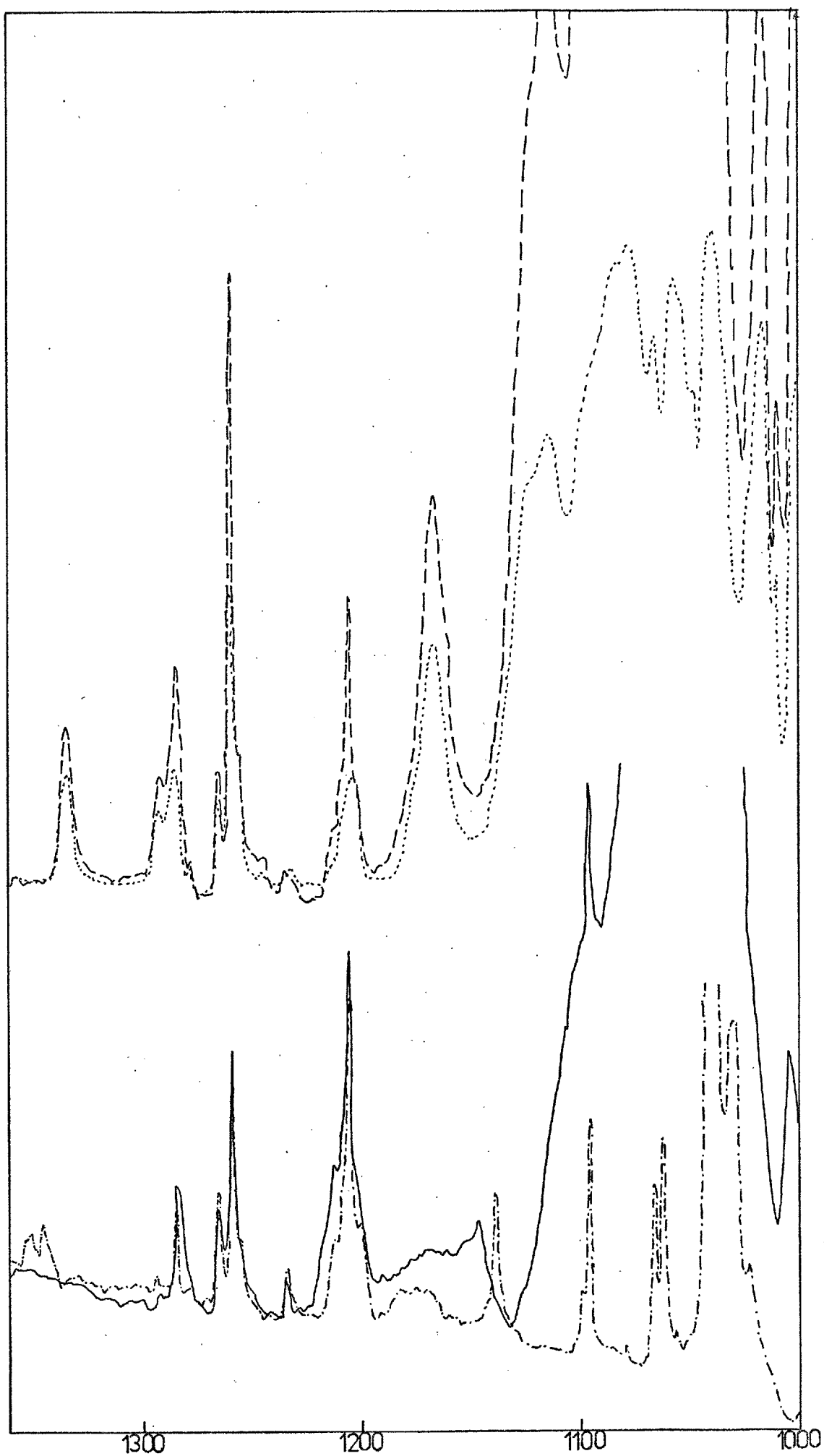
A2.2.5

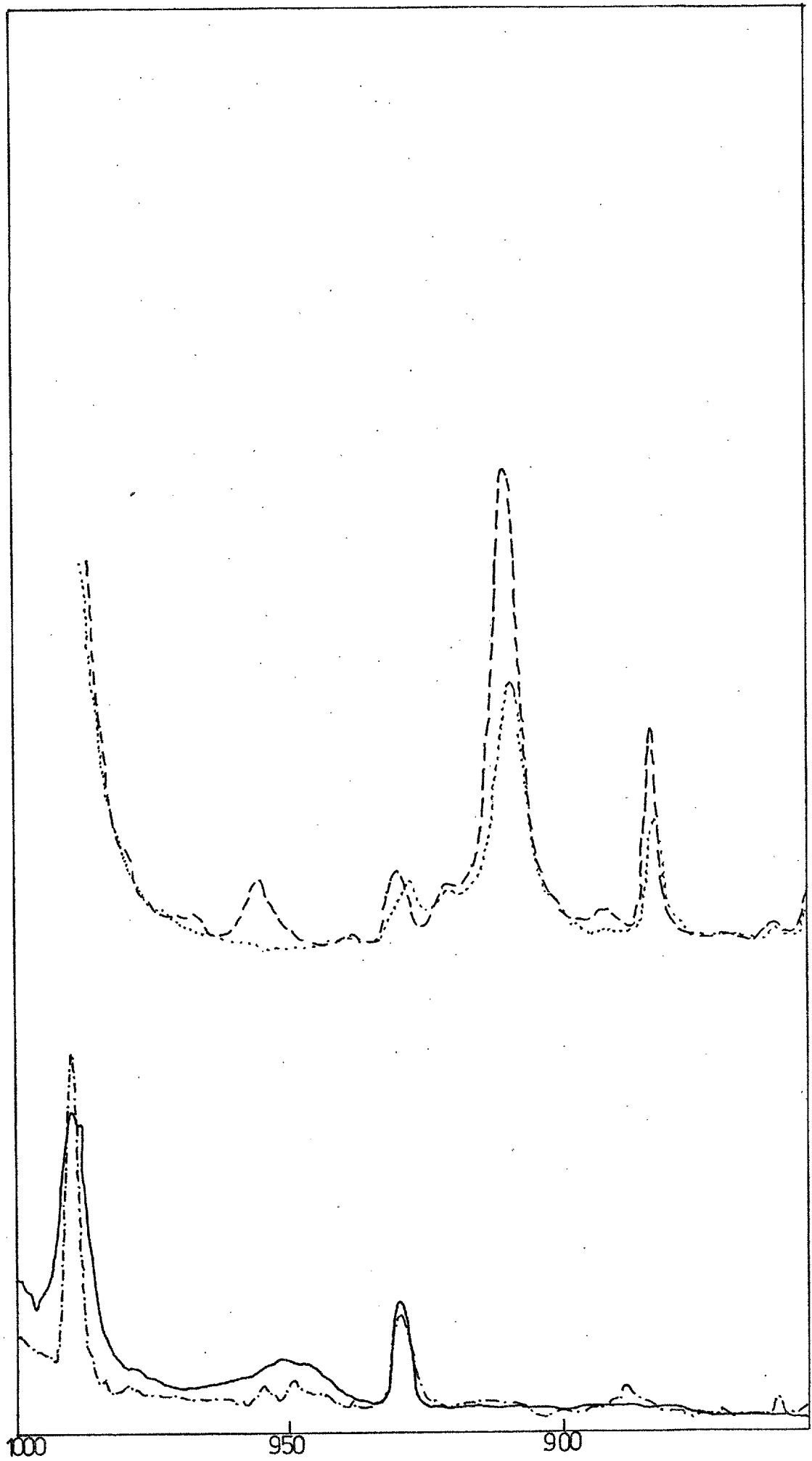


A2.3.1

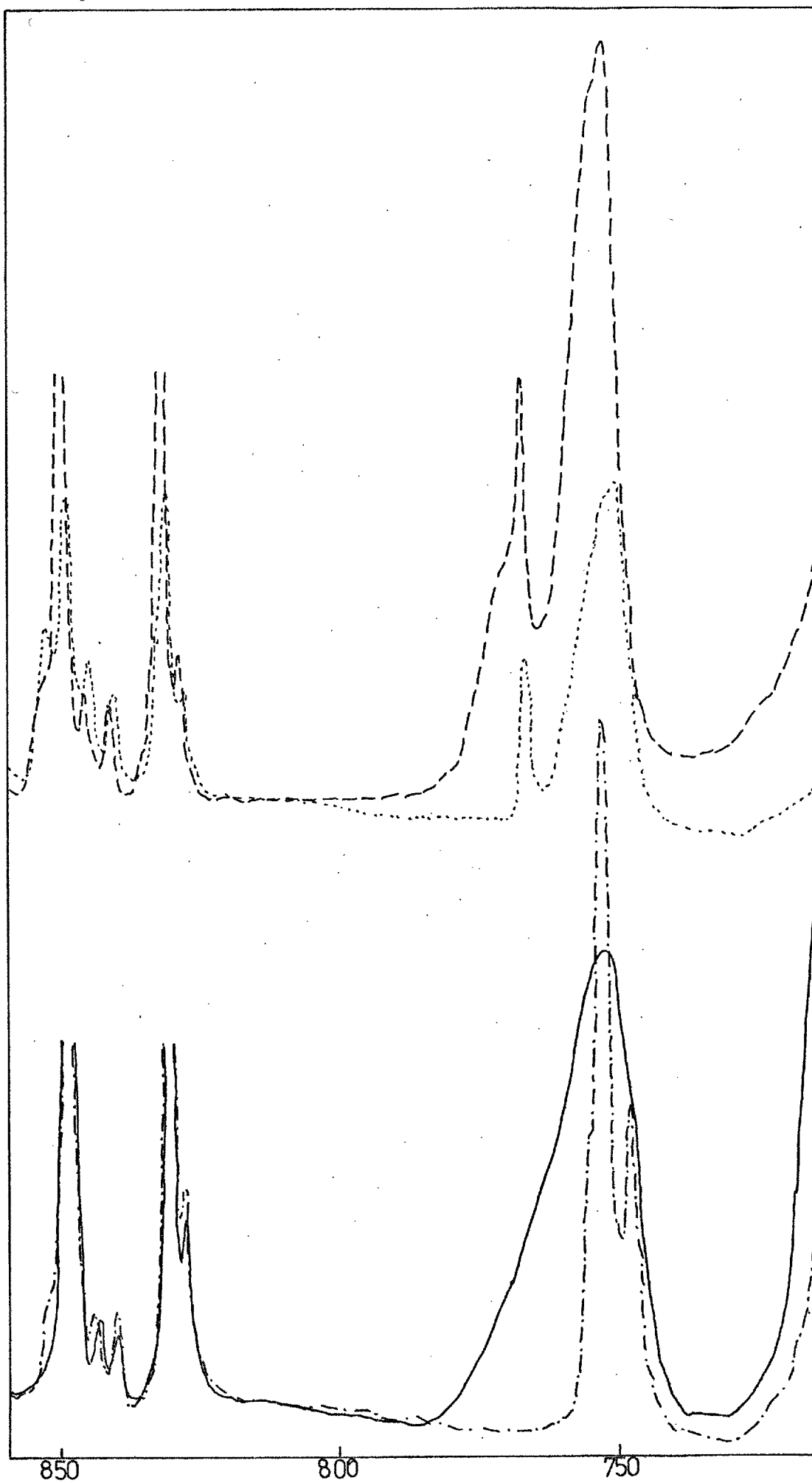


A2.3.2

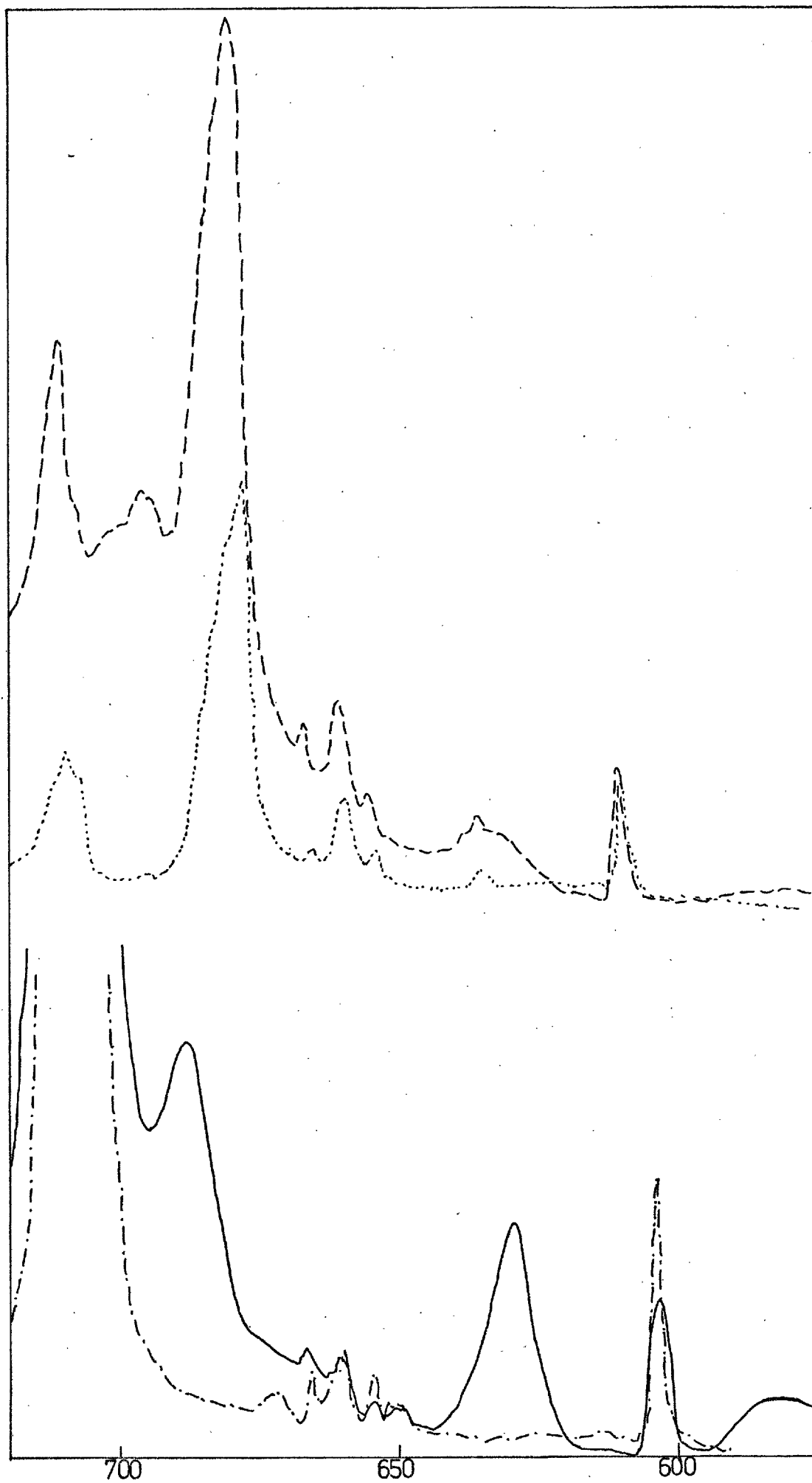




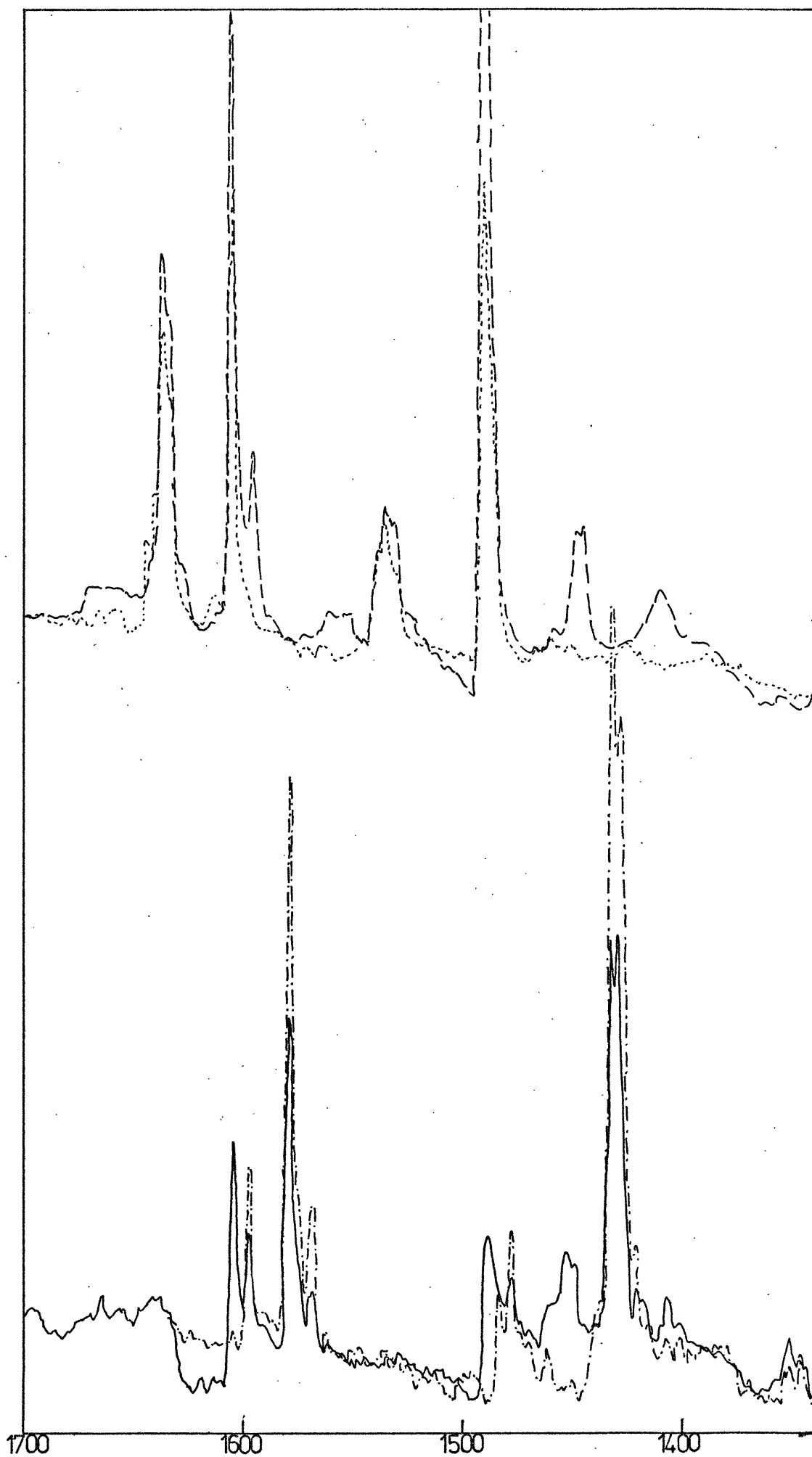
A2.3.4

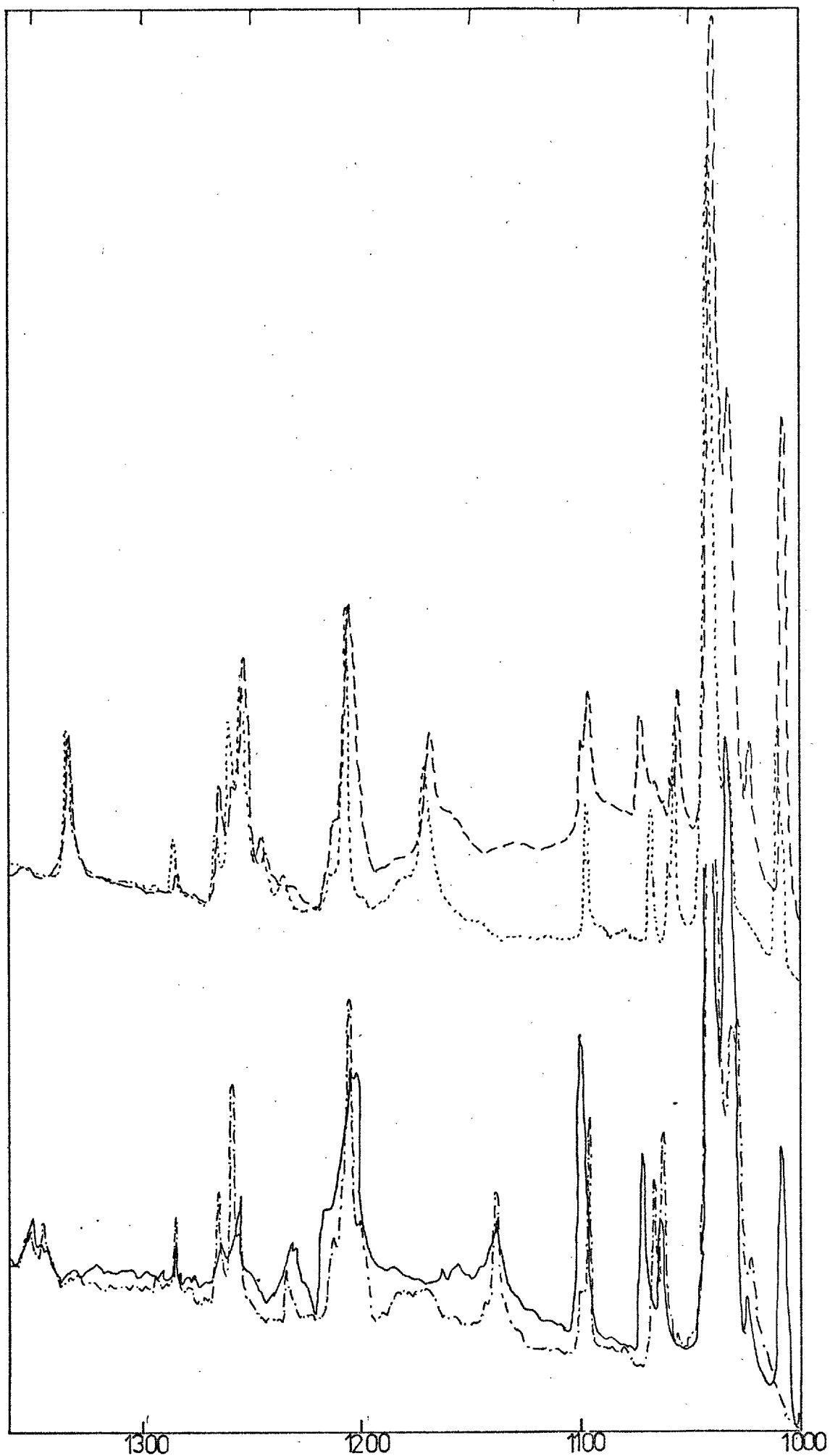


A2.3.5

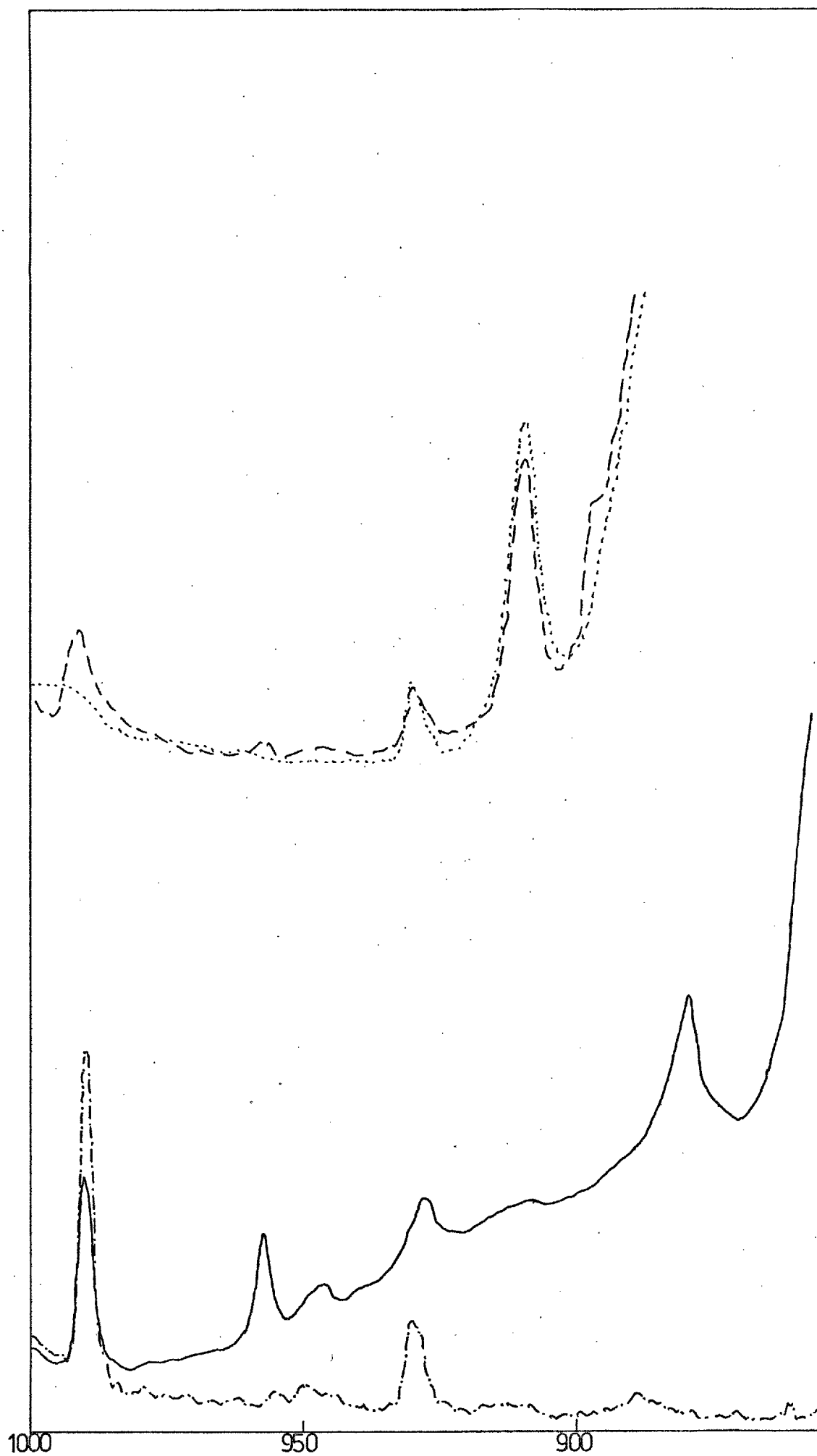


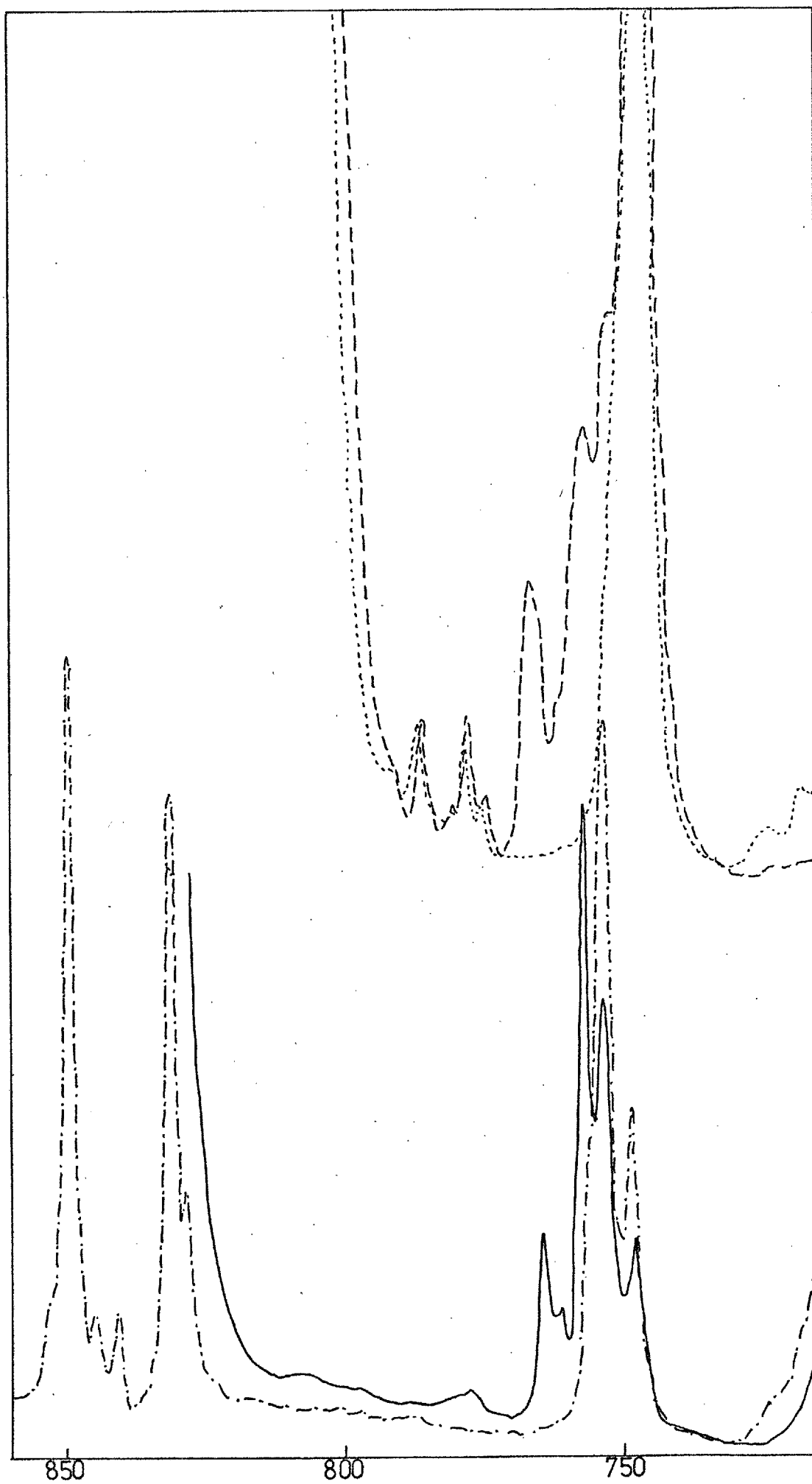
A2.4.1

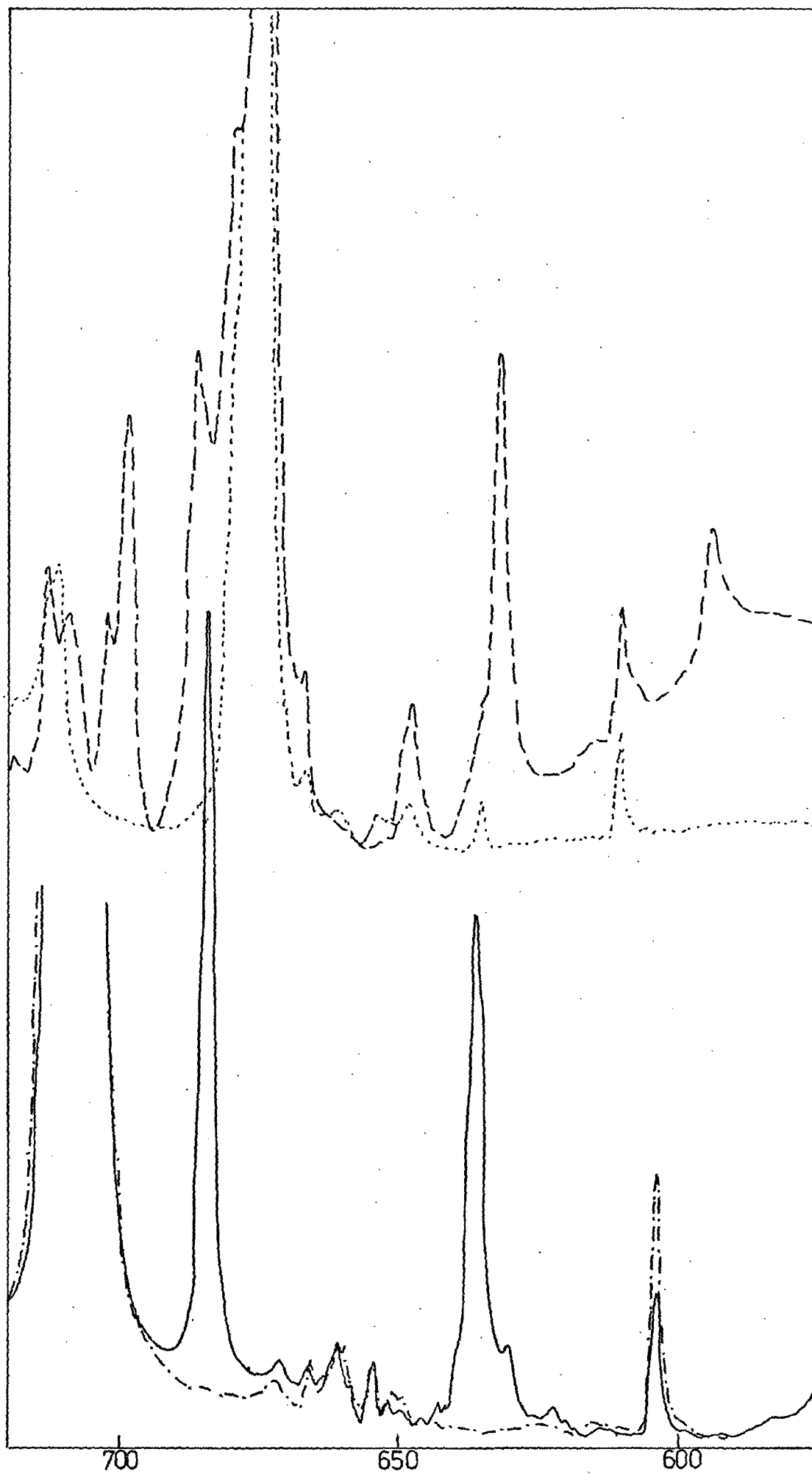


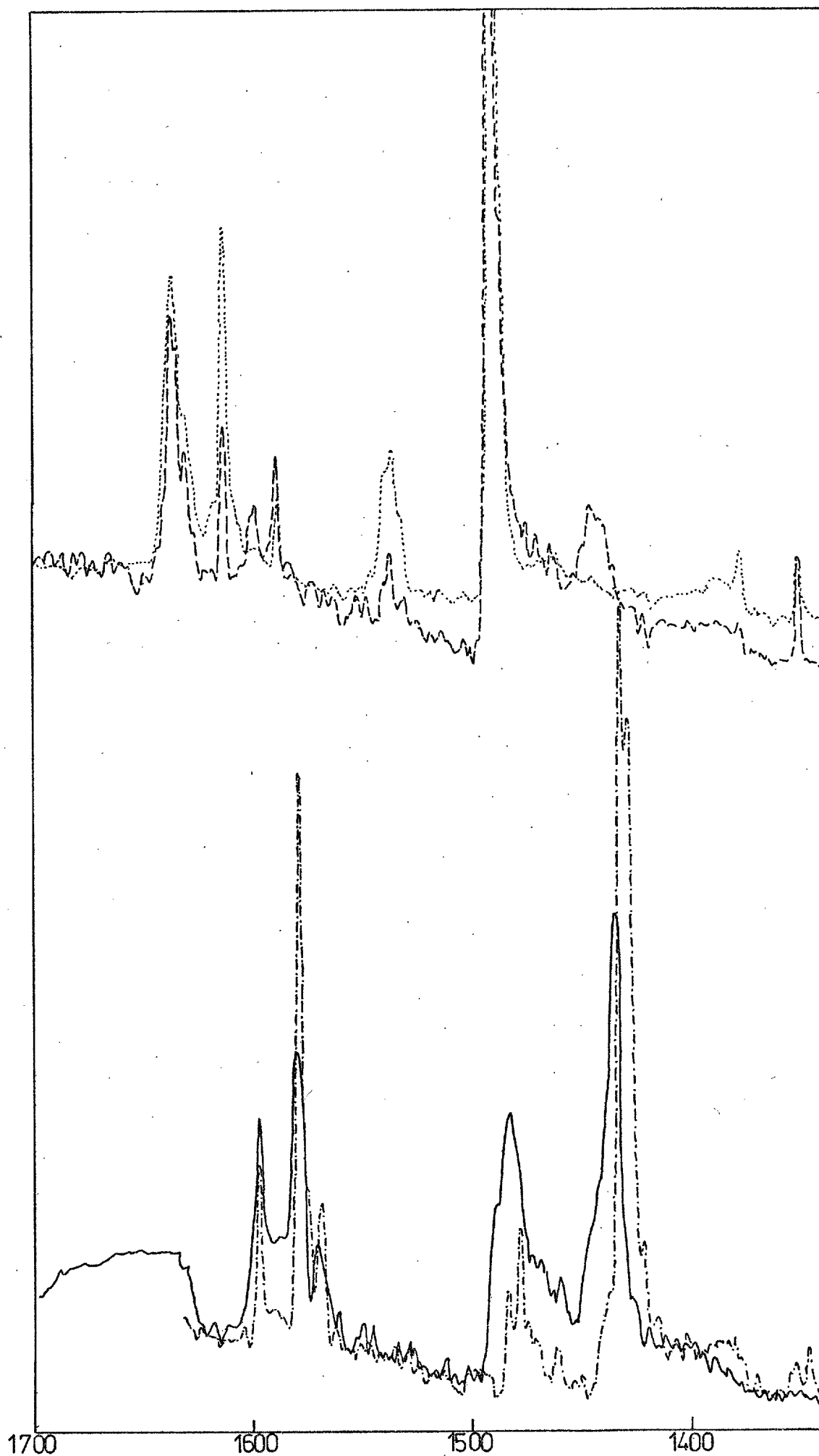


A2.4.3

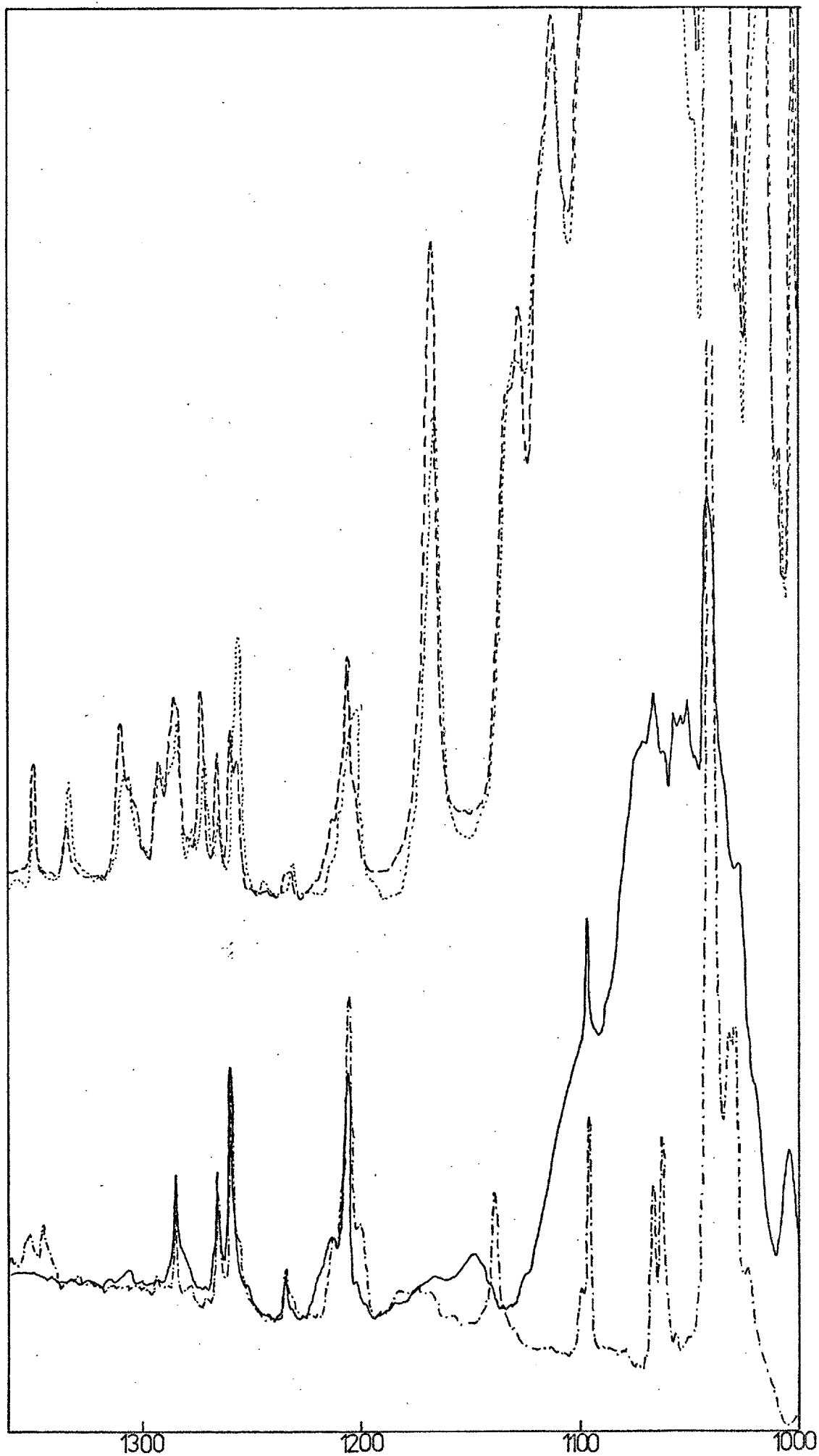




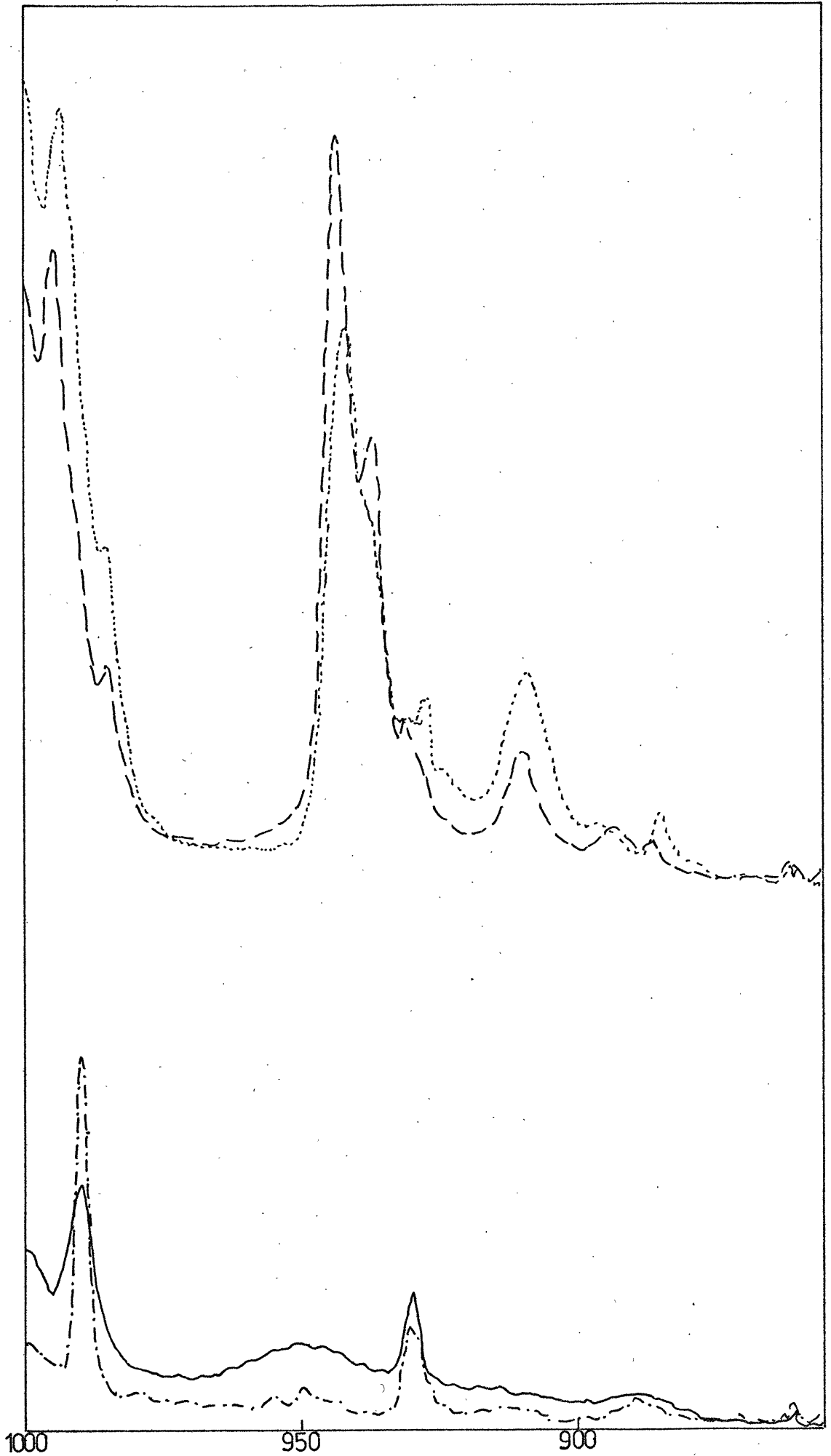




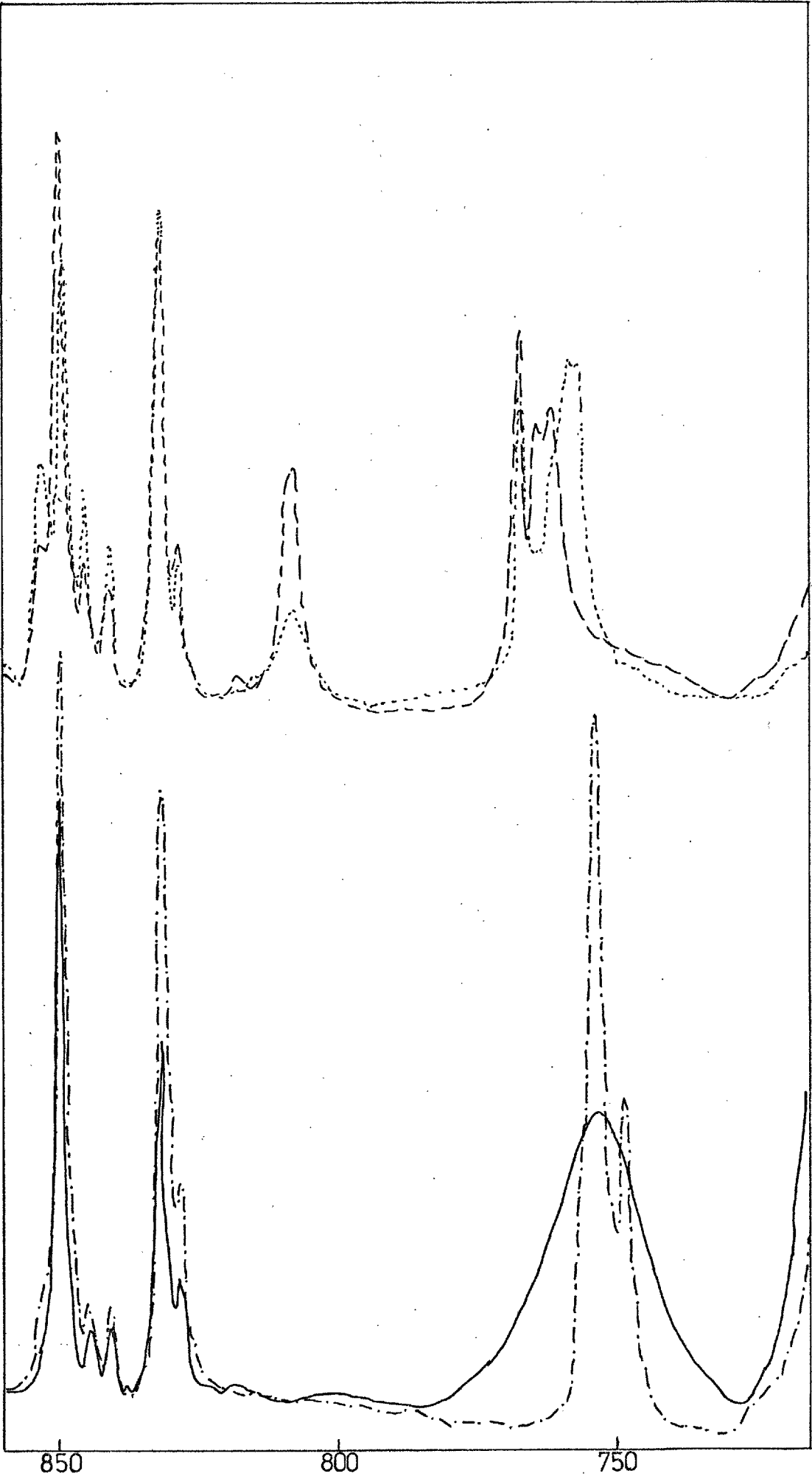
A2.5.2



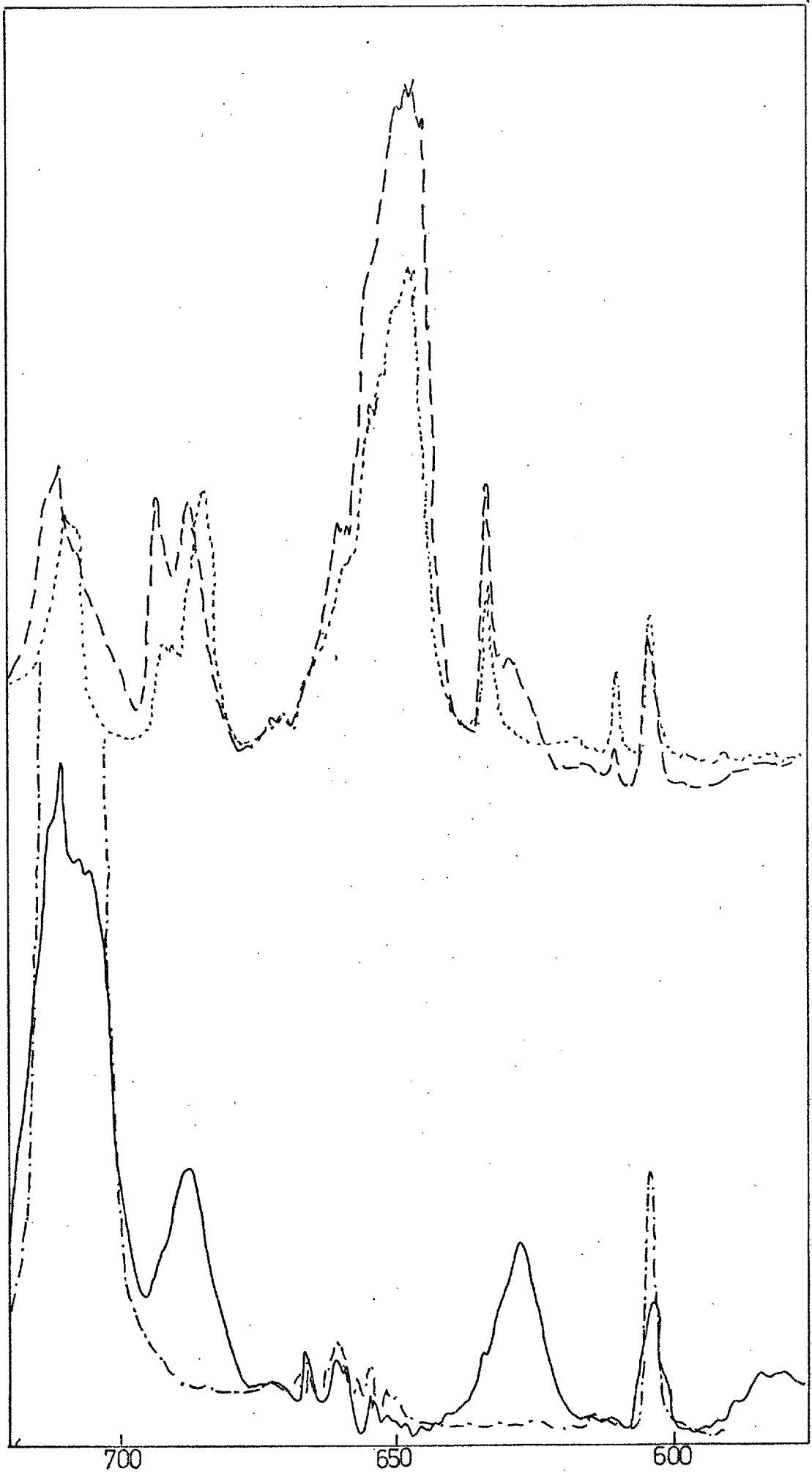
A2.5.3



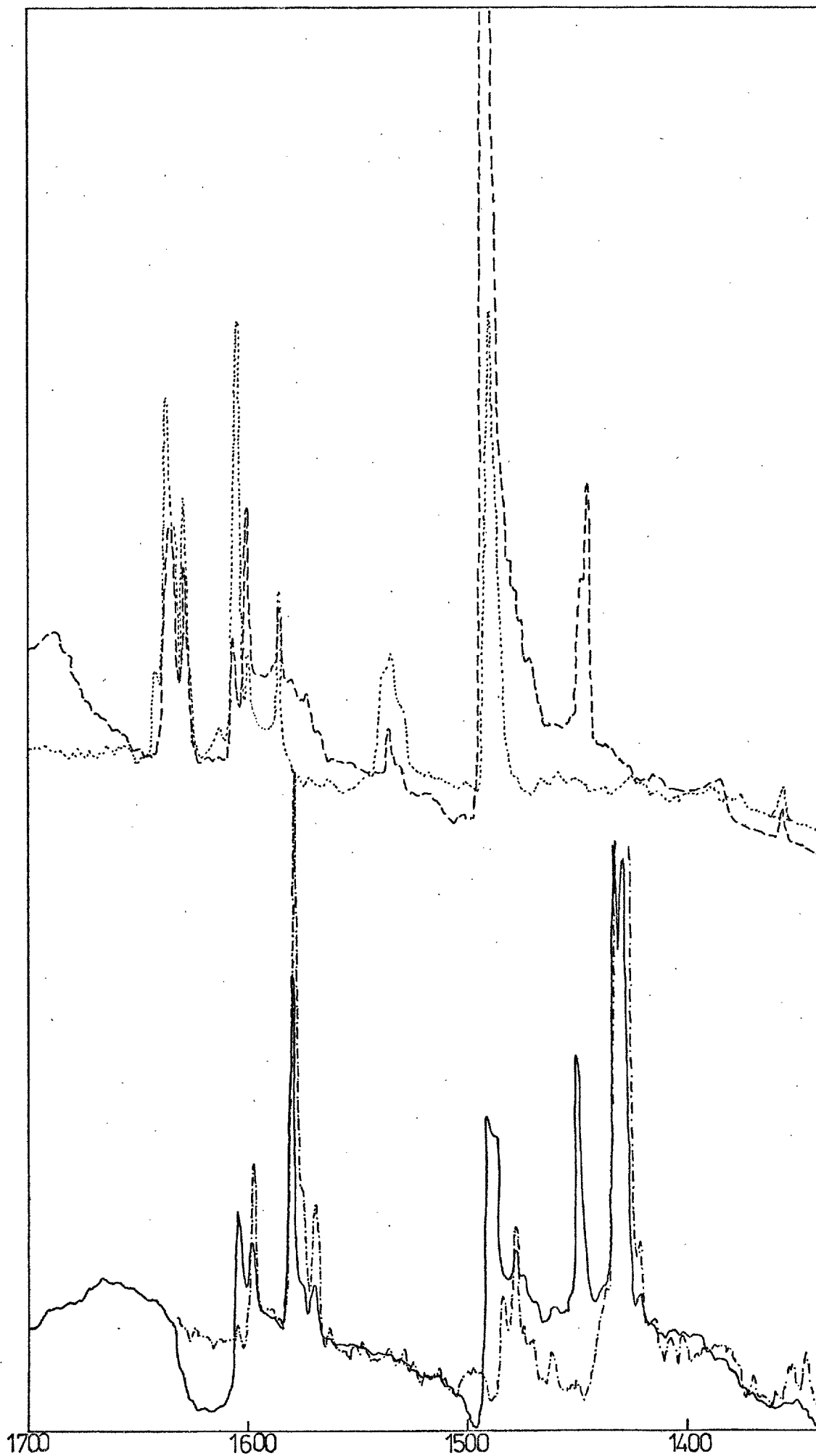
A2.5.4



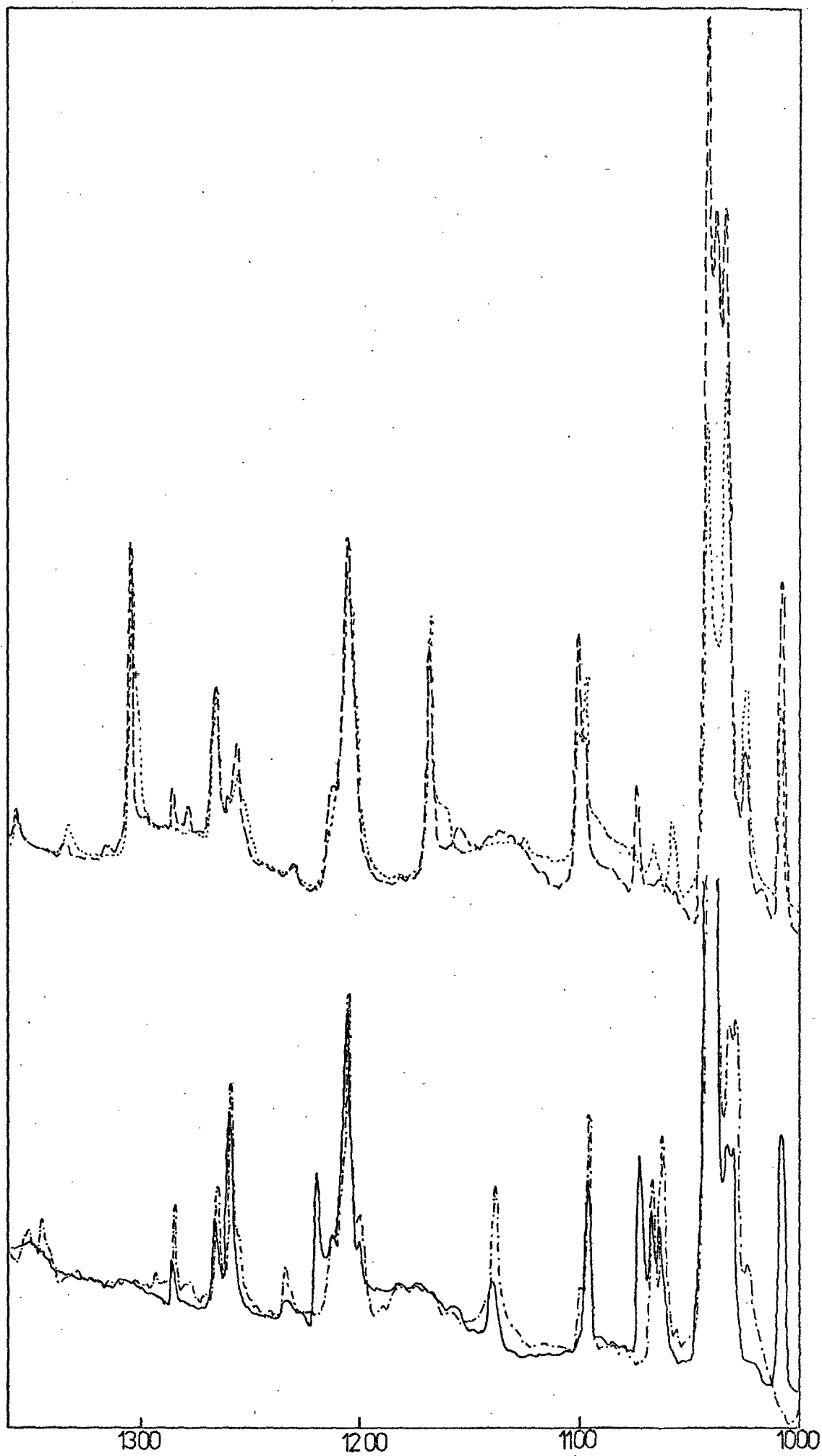
A2.5.5.



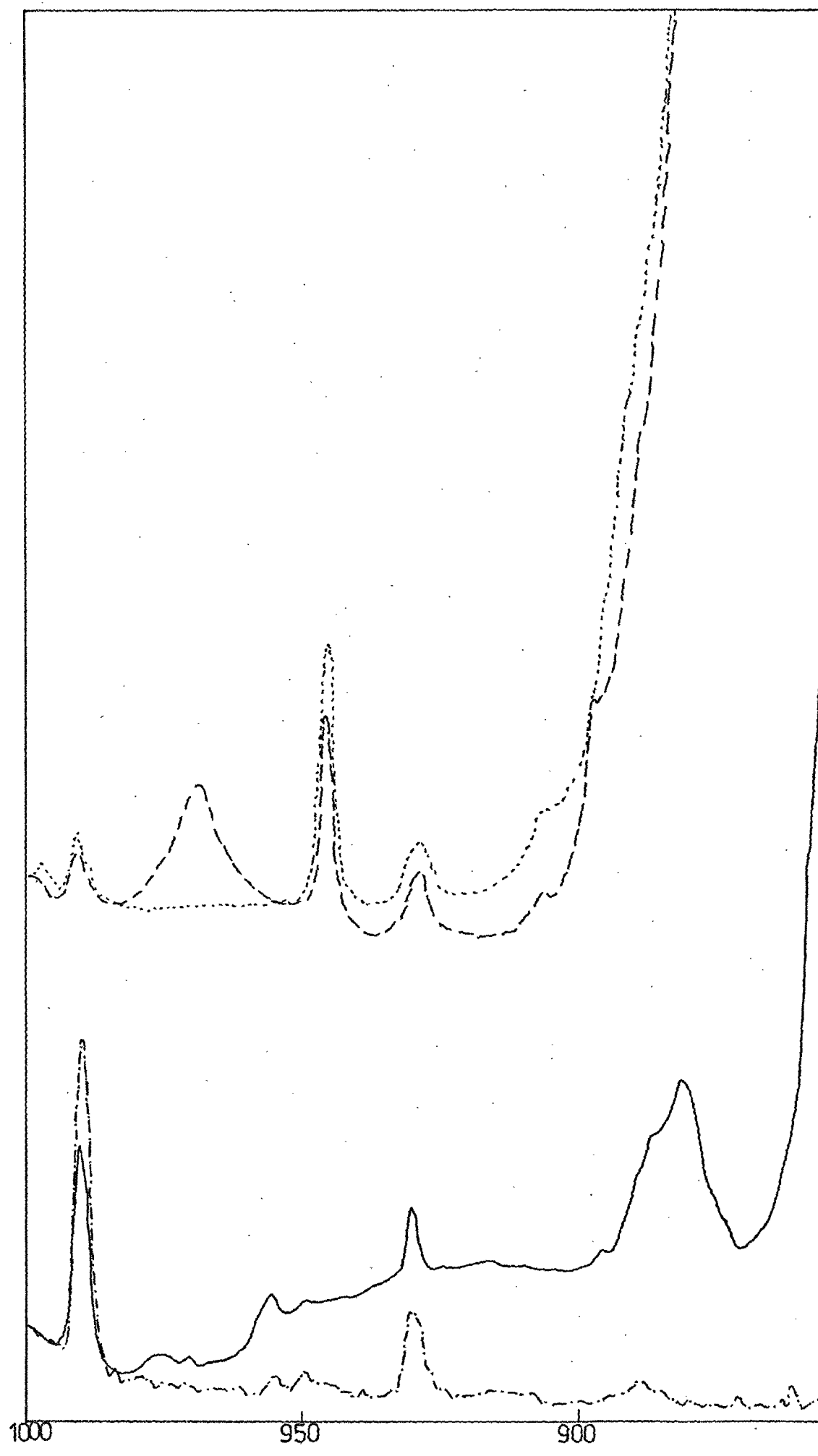
A2.6.1

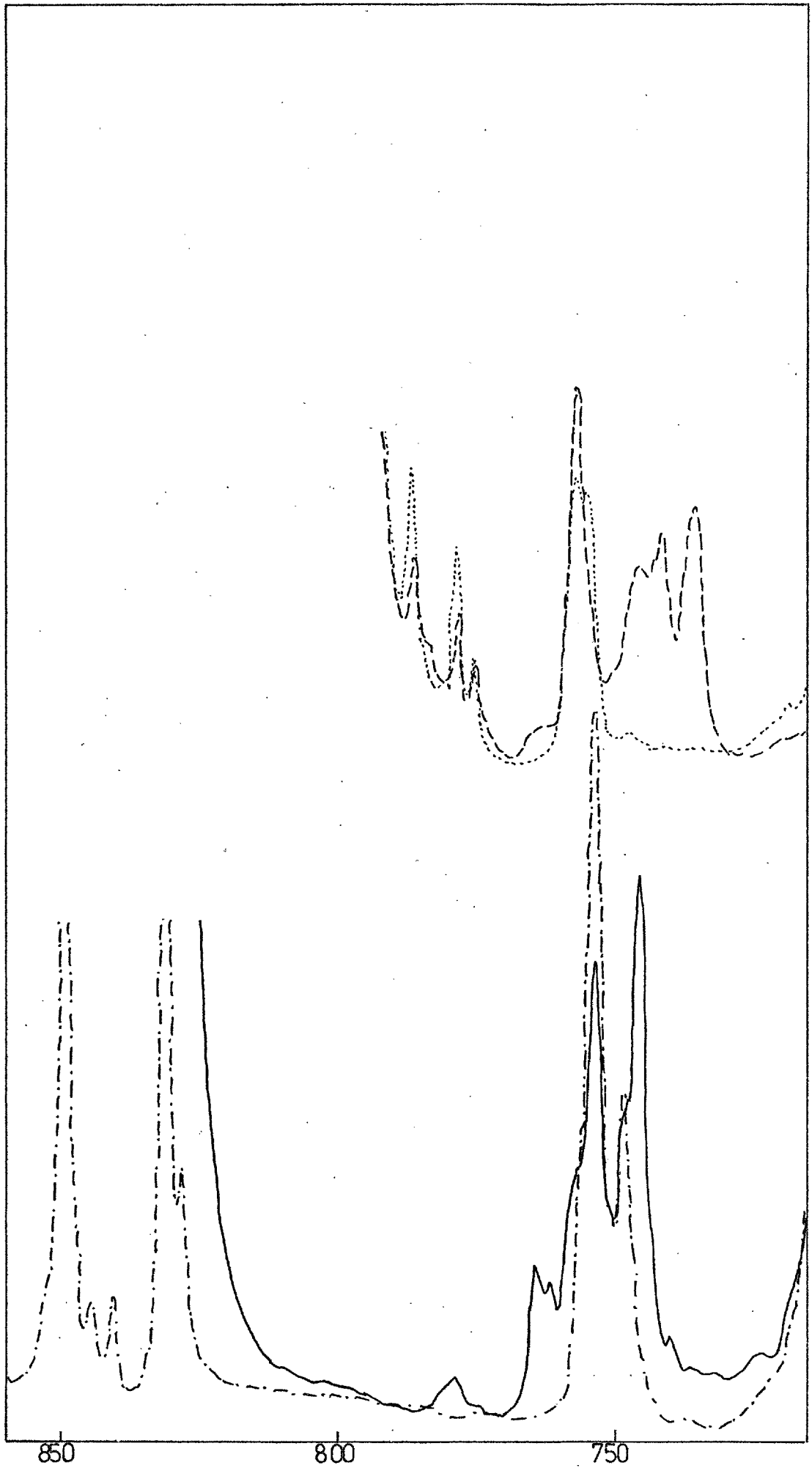


A2.6.2



A2.6.3





A2.6.5



REFERENCES

1. E.g. most recently :
 - (a) JOESTEN, M.D. and SCHAAD, L.J., "Hydrogen Bonding", Marcel Dekker (1974) and
 - (b) "The Hydrogen Bond", SCHUSTER, P., ZUNDEL, G. and SANDORFY, C. (eds.), North-Holland (1976).
2. WOOD, J.L., in "Spectroscopy and Structure of Molecular Complexes", J. Yarwood (ed.), Plenum Press (1973).
3. KOLLMAN, P.A. and ALLEN, L.C., J. Amer. Chem. Soc., 93, 4991 (1971).
4. MERLET, P., PEYERIMHOFF, S.D. and BUENKER, R.J., J. Amer. Chem. Soc., 94, 8301 (1972).
5. SABIN, J.R., Int. J. Quant. Chem. 2, 23, 31 (1968).
6. SCHUSTER, P., JAKUBETZ, W., BEIER, G., MEYER, W. and RODE, B.M., Jerusalem Symp. Quantum Chem. Biochem., 6, (Chem.Biochem.React., Proc.Int.Symp., 1973), 257 (1974).
7. BRICKMANN, J. and ZIMMERMANN, H., Ber. Bunsenges. Phys. Chem. 70, 157 (1966); 71, 160 (1967).
BEVAN, J.W., M.Sc. Thesis, Univ. of Surrey (1969).
8. SINGH, T.R. and WOOD, J.L., J. Chem. Phys., 48, 4567 (1968).
9. TAYYARI, S.F., Ph.D. Thesis, University of London, 1978.
10. SOMORJAI, R.L. and HORNIG, D.F., J. Chem. Phys., 36, 1980 (1962).
11. LIPPINCOTT, E.R. and SCHROEDER, R., J.Chem.Phys., 23, 1099 (1955); J.Phys.Chem., 61, 921 (1957).
12. DEAN, R.L. and WOOD, J.L., J.Mol.Struct., 26, 215 (1975).
13. ZIMMERMANN, H., Angew. Chem. (Int.Ed.), 3, 157 (1964).
14. CALDIN, E.F., Chem. Rev., 69, 135 (1969).
15. LEWIS, E.S., in "Proton Transfer Reactions", E.F. Caldin and V. Gold (eds.), Chapman and Hall (1975).

16. ROBINSON, B.H., in "Proton Transfer Reactions,
E.F. Caldin and V. Gold (eds.), Chapman and Hall (1975).
17. ROSENSTEIN, R.A., Ber. Bunsenges.Phys.Chem., 77,
493 (1973);
RÖSCH, N. and RATNER, M.A., J.Chem.Phys.,61, 3344
(1974);
JOHANSSON, A., Finn.Chem.Lett., 115 (1974).
18. WEIDEMANN, E., in Ref. 1(b), pp. 245-294.
19. JANOSCHEK, P., in Ref. 1(b), pp. 165-216.
20. BRZEZINSKI, B. and ZUNDEL, G., J. Chem. Soc.,
Faraday II, 72, 2127 (1976).
21. BORAH, B. and WOOD, J.L., Can.J.Chem., 54, 2470(1976).
22. KURZ, J.L. and KURZ, L.C., J. Amer. Chem. Soc., 94,
445 (1972);
CALDIN, E.F. and MATEO, S., J. Chem. Soc., Faraday I,
71, 1876 (1975).
CALDIN, E.F. and WILSON, C.J., Faraday Symp. Chem.
Soc., 10, 121 (1975).
23. COETZEE, J.F., CUNNINGHAM, G.P., McGUIRE, D.K. and
PADMANABHAN, G.R., Anal. Chem., 34, 1139 (1962);
COETZEE, J.F., Prog.Phys.Org.Chem., 4, 45 (1967).
24. PAULING, L., COREY, R.B. and BRANSON, H.R., Proc.
Nat. Acad. Sci., 137, 205 (1951);
PAULING, L. and COREY, R.B., Proc. Nat. Acad. Sci.,
137, 251 (1951).
25. WATSON, J.D. and CRICK, F.H.C., Nature, 171, 737,
964(1953); Proc. Roy. Soc. A223, 80(1954).
26. LÖWDIN, P.-O., Adv.Quant.Chem., 2, 213 (1966);
Ann. N.Y. Acad. Sci., 158, 86 (1969).
27. SCHULMAN, R.G., Ann.N.Y. Acad.Sci., 158, 96 (1969).
28. TAKAHASHI, H., MAMOLA, K. and PLYLER, E.K., J. Mol.
Spect., 21, 217 (1966).
29. WOOD, J.L., J.Mol.Struct., 13, 141 (1972); 16, 349
(1973).

30. HAMILTON, W.C. and IBERS, J.B., "Hydrogen Bonding in Solids", W.A. Benjamin (1968).
31. QUICK, A. and WILLIAMS, D.J., Can. J. Chem., 54, 2482 (1976).
32. PIMENTEL, G.C., J. Amer. Chem. Soc., 79, 3323 (1957).
33. SCOTT, R., PALMA, D. de and VINOGRADOV, S., J. Phys. Chem., 72, 3192 (1968);
SCOTT, R. and VINOGRADOV, S., J. Phys. Chem., 73, 1890 (1969).
34. SCHULMAN, S.G. and CAPOMACCHIA, A.C., J. Phys. Chem., 79, 1337 (1975).
35. MATAGA, N. and TSUNO, S., Bull. Chem. Soc. Japan, 29, 115 (1956);
MATAGA, N., Bull. Chem. Soc. Japan, 31, 481 (1958).
36. MATAGA, N. and TSUNO, S., Bull. Chem. Soc. Japan, 30, 711 (1957).
37. MATAGA, N. and KAIFU, Y., J. Chem. Phys., 36, 2804 (1962); Mol. Phys., 7, 137 (1963).
38. MATAGA, N., KAWASAKI, Y. and TORIHASHI, Y., Theoret. Chim. Acta, 2, 168 (1964).
39. INOUE, A., YOSHIHARA, K., KASUYA, T. and NAGAKURA, S., Bull. Chem. Soc. Japan, 45, 720 (1972).
40. WARE, W.R., SHUKLA, P.R., SULLIVAN, P.J. and BREMPHIS, R.V., J. Chem. Phys., 55, 4048 (1971);
LOKEN, M.R., HAYES, J.W., GOHLIKE, J.R. and BRAND, L., Biochemistry, 11, 4779 (1972);
OFRAM, M. and FEITELSON, J., Chem. Phys. Lett., 19, 427 (1963);
MATSUZAKI, A., NAGAKURA, S. and YOSHIHARA, K., Bull. Chem. Soc. Japan, 47, 1152 (1974).
41. DAVIS, J.C. and DEB, K.K., Adv. Mag. Res., 4, 201 (1970).
42. HOFACKER, G.L. and HOFACKER, U.A.H., Proc. Colloq. Ampère, 14, 502 (1966).
43. SAITO, H. and NUKADA, K., J. Amer. Chem. Soc., 93, 1072 (1971).

44. BONSOR, D.H., BORAH, B., DEAN, R.L. and WOOD, J.L.,
Can. J. Chem., 54, 2458 (1976).
45. BALDESCHWIELER, J.D. and RANDALL, E.W., Proc. Chem.
Soc., 303 (1961).
46. GRUNWALD, E. and RALPH, E.K., in "Dynamic Nuclear
Magnetic Resonance Spectroscopy", L.M. Jackman and
F.A. Cotton (eds.), Academic Press (1975).
47. Ref. 1(a), p. 42.
48. Ref. 1(a), pp. 241-246.
49. MULLER, N. and REITER, R.C., J.Chem. Phys., 42, 3265
(1965).
50. RANDALL, E.W. and GILLIES, D.G., Prog. N.M.R. Spec-
troscopy, J.W. Emsley, J. Feeney and L.H. Sutcliffe
(eds.), Pergamon Press, 6, 119 (1970).
51. KINTZINGER, J.P. and LEHN, J.M., Mol.Phys., 14, 133
(1968).
52. GIL, V.M.S. and MURRELL, J.N., Trans. Faraday Soc.,
60, 248 (1964)
53. SMITH, I.C. and SCHNEIDER, W.G., Can.J.Chem., 39,
1158 (1961);
KOTOWYCZ, G., SCHAEFER, T. and BOCK, E., Can. J. Chem.,
42, 2541 (1964).
54. MERRY, J.B. and GOLDSTEIN, J.H., J. Amer. Chem. Soc.,
88, 5560 (1966).
55. HATTON, J.V. and RICHARDS, R.E., Mol. Phys., 5, 153
(1962).
56. JOOP, V.N. and ZIMMERMANN, H., Z. Electrochem., 66,
440 (1962).
57. BENESI, H.A. and HILDEBRAND, J.H., J. Amer. Chem.
Soc., 71, 2705 (1949).
58. DERANLEAU, D.A., J.Amer.Chem.Soc., 91, 4044 (1969).
59. CLARKE, K. and ROTHWELL, K., J.Chem.Soc., 1885 (1960).
60. LINDEMANN, R. and ZUNDEL, G., J. Chem. Soc., Faraday
II, 68, 979 (1972); 72, 788 (1977).

61. MASON, S.F., in "Physical Methods in Heterocyclic Chemistry, Vol. II", A.R. Katritzky (ed.), Academic Press (1963).
62. MATAGA, N., KAIFU, Y. and KOIZUMI, M., Bull.Chem. Soc. Japan, 29, 373 (1956);
MATAGA, N. and TSUNO, S., Bull.Chem. Soc. Japan, 30, 368 (1957);
MATAGA, N. Bull. Chem. Soc. Japan, 31, 459 (1958);
El SAYED, M., J. Chem. Phys., 36, 573 (1962);
MOOMAW, W.R. and ANTON, M.F., J. Phys. Chem., 80, 2243 (1976).
63. PARKER, C.A., "Photoluminescence of Solutions", Elsevier, pp. 220-234 (1968).
64. STERN, O. and VOLMER, M., Phys.Z., 20, 183 (1919).
65. QUICK, A. and WILLIAMS, D.J., Can. J. Chem., 54, 2465 (1976).
66. CLEMENTS, R.D., Ph.D. Thesis, Univ. of London (1973).
67. FOGLIZZO, R. and NOVAK, A., J. Chem. Phys., 50, 5366 (1969).
68. CASTELUCCI, E., SBRANA, G. and VERDERAME, F.D., J.Chem. Phys., 51, 3762 (1969).
69. CLEMENTS, R.D. and WOOD, J.L., J. Mol. Struct., 17, 265 (1973).
70. GREEN, J.H.S., KYNASTON, W. and PAISLEY, H.M., Spec. Acta, 19, 549 (1963).
71. COOK, D., Can. J. Chem., 39, 2009 (1961).
72. FOGLIZZO, R. and NOVAK, A., J. Chim. Phys., 66, 1539 (1969).
73. CORRSIN, L., FAX, B.J. and LORD, R.C., J. Chem. Phys., 21, 1170 (1953).
74. CLEMENTS, R.D., DEAN, R.L. and WOOD, J.L., J. Mol. Struct., 17, 291 (1973).
75. SPINNER, E., J. Chem. Soc., 3680 (1963).
76. ALBERT, A. in "Physical Methods in Heterocyclic Chemistry, Vol.I", A.R. Katritzky (ed.), Academic Press (1963).

77. KREEVOY, M.M. and MEAD, C.A., J. Amer. Chem. Soc., 84, 4596 (1962).
78. YARWOOD, J. in "Spectroscopy and Structure of Molecular Complexes", J. Yarwood (ed.), Plenum Press (1973).
79. YARWOOD, J., Trans. Faraday Soc., 65, 934 (1969).
80. BOOBYER, G.J. and ORVILLE-THOMAS, W.J., Spec. Acta, A22, 147 (1966).
81. LONG, D.A. and THOMAS, E.L., Trans. Faraday Soc., 59, 783 (1963).
82. YARWOOD, J. and ROBERTSON, G.N., Nature, 257, 41 (1975).
YARWOOD, J. and ROBERTSON, G.N., Mol. Phys., to be published.
YARWOOD, J., ACKROYD, R. and ROBERTSON, G.N., Mol. Phys., to be published.
83. Ref. 2, p. 339.
84. CHENON, B. and SANDORFY, C. Can.J.Chem., 36, 1181 (1958).
EBSWORTH, E. and SHEPPARD, N., Spec. Acta, A13, 261 (1959).
MATHIEU, J.P. and POULET, H., Spec. Acta, A16, 696 (1960).
85. McGAW, B.L. and IBERS, J.A., J.Chem.Phys., 39, 2677 (1963).
86. LEE, J.D. and WALLWORK, S.C., Acta Cryst., 19, 311 (1965).
87. MEDHI, K.C., Opt. i Spekt., 19, 49 (1965) [translated in Optics and Spect. 19, 24 (1965)].
88. GREEN, J.H.S., HARRISON, D.J., KYNASTON, W. and PAISLEY, H.M., Spec. Acta, A26, 2139 (1970).
89. WILSON, E.B., Phys. Rev., 45, 706 (1934).
90. LONG, D.A., MURFIN, F.S. and THOMAS, E.L., Trans. Faraday Soc., 59, 12 (1963).
91. DEAN, R.L. Ph.D. Thesis (Appendix 2), University of London (1974).
92. CLEMENTS, R.D. and WOOD, J.L., J. Mol. Struct., 17, 283 (1973).

93. CHUCK, R.J., Ph.D. Thesis, University of London (1966).
94. PRICE, R., Ph.D. Thesis, University of London (1969).
95. LICHTER, R.L. and ROBERTS, J.D., J. Amer. Chem. Soc., 93, 5218 (1971).
96. IRVING, C.S. and LAPIDOT, A., J. Chem. Soc., Chem. Comm., 184 (1977)
97. KAWANO, K., OZAKI, Y., KYOGOKU, Y., OGOSHI, H., SUGIMOTO, H. and YOSHIDA, Z., J. Chem. Soc., Chem. Comm., 226 (1977).
98. HAWKES, G.E., LITCHMAN, W.M. and RANDALL, E.W., J. Mag. Res., 19, 255 (1975).
99. LICHTER, R.L. and ROBERTS, J.D., J. Amer. Chem. Soc., 93, 3200 (1971).
100. MÜLLEN, K. and PREGOSIN, P.A., "Fourier transform N.M.R. techniques : a practical approach", Academic Press (1976).
101. WILMSHURST, J.K. and BERNSTEIN, H.J., Can. J. Chem., 35, 1183 (1957).
102. CLEMENTS, R.D. and WOOD, J.L., J. Mol. Struct., 17, 291 (1973).
103. BORAH, B. and WOOD, J.L., J. Mol. Struct., 22, 237 (1974).
104. EFIMOV, Y.Y. and NABERUKHIN, Y.I., Mol. Phys., 30, 1621, 1627 and 1635 (1975); 33, 759 and 779 (1977).
105. MARQUARDT, D.W., J. Soc. Ind. Indust. Appl. Math., 11, 431 (1963).