



The University of Reading

**Using Matrix Isolation-FTIR
for
Trace Atmospheric Gas Analysis**

**A thesis submitted for the degree of
Doctor of Philosophy**

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Abstract

The matrix isolation technique combined with FTIR spectroscopy has been used for trace atmospheric gas analysis. The main objective was to develop this technique into a simple, reliable field method using the simplest possible apparatus to give reliable results. As a preliminary to the research, calibration curves of the intensity of IR absorptions of acetone, acetaldehyde, acetic acid, formic acid, N_2O , SO_2 and ethylene were constructed for a range of concentrations of these reagents in CO_2 . All spectra were recorded on solid films at 77 K. Linear responses were observed for absorbance vs. concentration and the technique showed the best sensitivity for N_2O which was detected at a minimum atmospheric concentration of ca. 32.5 ppb. Acetone, acetaldehyde, acetic acid and ethylene were detected at a minimum atmospheric concentration of ca. 3.3 ppm while formic acid was detected at a minimum atmospheric concentration of ca. 2.3 ppm. SO_2 was detected at a minimum atmospheric concentration of ca. 325 ppb.

A thorough spectroscopic study was done on some carbonyl compounds in CO_2 matrices including the effect of CO_2 matrix on the IR spectra as in most cases spectra have never previously been recorded for these species in CO_2 matrices. Another study of some isotopic species of these compounds in CO_2 matrices was then done to see the presence of any interaction between the compounds and CO_2 matrix which could lead to slightly different spectra from those of the gas-phase or even from the spectra of the same compounds isolated in different matrices which have been reported in other studies.

A new method for infrared analysis of multicomponent gas mixtures which involves a condensed phase sampling technique employing commercially available cryogenic equipment is described. Molecules are characterized by a small number of well defined infrared absorptions. As a method of pre-concentrating the atmospheric carbonyl compounds, different adsorbent materials were studied and from them the activated carbon was chosen as it gave the best recoveries (85-91%) and selectivity. The MI-FTIR technique combined with the adsorbent tubes was used in the field work for sample collection and analysis. The method permits analyses to be executed rapidly and is capable of creditable quantitative results. The results are encouraging indicating that this sampling method provides a practicable basis for chemical analysis of these compounds.

To my husband Adel

for his unlimited love, trust, patience, concern and encouragement.

Words would never express my great gratitude, appreciation and thanks to him.

His love pulled me together in moments of weakness and depression.

To him I dedicate this work.

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Chapter 1 Introduction

The major part of this thesis is devoted to studies of the infrared spectra of some carbonyl compounds, which may be present as atmospheric pollutants, and their isotopic derivatives in CO₂ matrices. Accordingly in this introductory chapter, the interest in the air pollution, the matrix isolation (MI) technique and its application in the analysis of trace atmospheric gases are reviewed.

1.1 Air Pollution

People's interest in the atmosphere is probably as old as the history of mankind. Certainly there are few other aspects of our physical environment that affect our daily lives more than the phenomena we collectively call the weather. Air pollution and its control is very important and some cases perhaps even vital. Hence, there is a need for increased awareness and understanding of the atmosphere composition. The atmosphere is a mixture of many discrete gases, each with its own physical properties, in which varying quantities of tiny solid and liquid particles are suspended.¹

Air pollution has become a growing threat to our health and welfare because of the increasing emissions of air contaminants into our atmosphere. An average adult male requires about 13.5 kilograms of air each day. The cleanliness of air, therefore, should certainly be very important to us. Air is never perfectly clean. There have always been many natural sources of air pollution. Ever since people have been on earth, however, they have added to the frequency and intensity of some of these natural pollutants.¹

1.2 Atmospheric Components

1.2.1 Atmospheric CO₂

Although only about 0.035% (350 ppm) of air consists of CO₂, it is the atmospheric non-pollutant species of most concern.² CO₂, along with water vapour, is primarily responsible for the absorption of infrared energy re-emitted by the Earth so that some of this energy is reradiated back to the Earth's surface. Current evidence suggests that changes in the atmospheric carbon dioxide level will substantially alter the Earth's climate through the greenhouse effect.

1.2.2 Carbonyl Compounds

Aldehydes

Carbonyl compounds, primarily formaldehyde (HCHO) and acetaldehyde (CH₃CHO) are key components of photochemically generated air pollution.^{3,4} The sources of carbonyl compounds are both primary (directly emitted) and secondary (formed in the atmosphere). Several recent reviews have described the mechanism by which formaldehyde and acetaldehyde are formed in the atmosphere.⁵⁻⁷ Primary emission sources of these carbonyl compounds include motor vehicles. Motor vehicle emissions of formaldehyde, and for some fuels acetaldehyde, have been shown to increase with the use of oxygenated fuels, including methanol, ethanol, and methyl tertiary butyl ether (MTBE) blended fuels.⁸

1.2.3 Ketones

Acetone was found to be the dominant nonmethane organic species present in the atmosphere sampled primarily over eastern Canada.⁹ A concentration range of 357 to 2310 part per trillion (ppt), i.e., 1 μg in 1000 kg, with a mean value of 1140 ± 413 ppt was measured. Under extremely clean conditions, generally involving Arctic flows, lowest (background) mixing ratios of 550 ± 100 ppt were present in much of the troposphere studied. A substantial global source in the vicinity of 40-60 Tg/yr is estimated to be present. It is suggested that nonmethane hydrocarbon oxidation, biomass burning, and direct biogenic emissions are important sources of acetone.

1.2.4 Sulfur-Containing Compounds

Sulfur-containing compounds are emitted naturally to the Earth's atmosphere from oceans, soils and plants, and as a result of weathering of continental crusts, eruptions of the industrial revolution, human influences (e.g. the combustion of fossil fuels, industrial processes, biomass burning, agricultural activities, waste incineration and the use of explosives) have continuously added more sulfur to the atmosphere, thereby perturbing its natural cycle.¹⁰ Atmospheric sulfur compounds are major contributors to acidic deposition and also endanger the ozone layer as they reach the stratosphere.

Sulfur dioxide (SO_2) derived from the combustion of sulfur in fossil fuels is major air pollutant in urban areas of the world.¹¹ Sulfur oxides (SO_x ; $x = 2$ or 3) are parts of a complex pollutant mixture. SO_2 is a colourless gas that reacts on the surface

of a variety of airborne solid particles. It is readily soluble in water and can be oxidized within airborne water droplets. SO₂ results from the combustion of sulfur-containing ores, and the other industrial processes. Domestic fires can also produce emissions containing sulfur dioxide.

Sources of SO₂

While there are some natural sources of sulfur dioxide (such as volcanoes) that contribute to environmental levels, man-made contributions from the combustion of fossil fuels are of prime concern in relation to human exposures. Over the past 10-20 years there has been a tendency towards declining emissions in much of the European Region, due to changes in the types or amounts of fuel used. More importantly, however, the types of sources have changed even more, away from small multiple sources (domestic, commercial or industrial) towards large single sources such as power stations, which disperse pollutants at higher altitudes. The net result has been a marked reduction in concentrations of sulfur dioxide in many large cities that were at one time highly polluted. A more widespread distribution, by long-distance transport within the region, is now the dominant pattern.

Occurrence of SO₂ in Air

As a result of the changes in sources, annual mean levels of SO₂ in major cities of Europe, stated earlier by WHO to be within the range 100-200 µg/cm³, are now largely below 100 µg/cm³. Similarly, there has been a decline in maximum daily mean values, which are now mainly in the range 250-500 µg/cm³. Indoors concentrations of

SO₂ are generally lower than outdoor concentrations, since absorption of SO₂ occurs on walls, furniture, clothes and in ventilation systems.

1.2.5 Nitrogen Oxides

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N₂O), nitric oxide (NO), and nitrogen dioxide (NO₂).¹¹ Microbially generated nitrous oxide is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its concentration decreases rapidly with altitude in the stratosphere due to the photochemical reaction:



and some reactions with singlet atomic oxygen:



These reactions are significant in terms of depletion of the ozone layer. Increased global fixation of nitrogen, accompanied by increased microbial production of N₂O, could contribute to ozone layer depletion.

1.3 Measurement of Air Pollution

The measurement of ambient concentrations of atmospheric pollutants is usually carried out for either routine monitoring or scientific research on the processes which are responsible for the emissions, transformations, transport and deposition of atmospheric pollutants. The monitoring activities require methods and instrumentations which should ensure maximum field reliability even when precision and accuracy are

known at the optimum level. In scientific work, the need for accurate and precise measurements is mandatory if reliable measurements must be carried out.¹² In order to obtain detailed information about the level of pollutant concentrations, sensitive and reliable measuring techniques are needed.

Ambient air analysis is a rapidly changing field where new technology is constantly being developed and applied. However, the following basic precepts of analytical chemistry are still applied:¹³

- accurate standards are required to perform accurate analyses.
- calibration should be performed in the same way as analysis.
- sample alteration should be as little as possible before analysis.
- cleanliness and control of both sampling and analytical parameters are essential.
- quality control and quality assurance are critical for documenting the quality of analytical data.
- contamination must be avoided in order to generate valid field data.

1.4 Analytical Techniques for Air Pollution

Infrared (IR) Spectroscopy is one of the most powerful techniques available to analytical chemists. It serves both research applications and the more routine studies conducted in applications and process control laboratories. Furthermore, infrared analysis is applicable to both qualitative and quantitative analysis.¹⁴ IR spectroscopy, however, suffers the lack of sensitivity due to relatively low absorption strengths, weak sources and relatively poor detectors. Ultra-violet (UV)/visible spectroscopy has better sensitivity, sources and detectors but not good selectivity due to the broadness of many

UV/visible spectra. Gas chromatography (GC) has its own problems since while sensitivity is very high it is applicable only to certain classes of compounds.

1.5 FTIR-MI Technique

Gas phase Fourier Transform Infrared spectroscopy (FTIR) is often used in the analysis of trace impurities in high-purity gases. However, interference could occur if the main gas shows infrared active vibrations.¹⁵ This problem may be solved using the matrix isolation (MI) technique first proposed by Whittle *et al.*¹⁶ as a potential method of isolating radicals and other reactive species for spectroscopic examination. In matrix isolation the active molecules are trapped in a solid matrix of inert material at a low temperature. The low temperature will inhibit molecular rotation of most molecules so the IR spectrum is mainly due to vibrational transition;¹⁷ thus sharp absorption bands are achieved. The molecules are isolated from one another by the inert matrix and can be detected by FTIR with minimum interference. This isolation of molecules and the sharpness of the spectral bands also allow the study of many species simultaneously in the same sample.

The matrix isolation method can be used when it is difficult by other methods to maintain a suitable concentration of free radicals and other unstable substances since it involves accumulation of a reactive substance under conditions which prevent reaction. This can be done by spraying a gas mixture of the matrix gas and the active species onto a surface cold enough to condense the matrix immediately. If the mole ratio of matrix to active substance (M/A) is sufficiently large, the matrix will isolate trapped molecules and prevent recombination reactions.¹⁶

The matrix isolation technique combined with FTIR spectroscopy has been used for atmospheric trace gas analysis.¹⁷ Griffith has described a method in which atmospheric samples are cryogenically collected at 77 K in the form of a solid matrix of atmospheric CO₂ containing the condensable trace gases, and analysed by FTIR absorption spectroscopy.

1.6 Matrix Material

The utility of a matrix material depends on several properties. The matrix must be inert with respect to reaction with the active species. A rare gas is ideal in this respect. Some materials may be acceptable as matrices for certain active substances and not for others. The matrix must also be sufficiently rigid to prevent diffusion of the active species. The marked effect of temperature on diffusion makes the suitability of a given matrix highly temperature dependent. Another important point is that the matrix must have no absorptions in the spectral region of interest. Even a weak absorption band can interfere at a high mole ratio of matrix to active material. Nitrogen and hydrogen are transparent through all spectral regions except the far ultraviolet and some substances such as carbon dioxide leave large portions of the infrared spectrum relatively free.

Since the matrix and active materials are mixed in the gas phase and sprayed onto a cold window suspended in a vacuum shroud, the matrix material must have a sufficiently high vapour pressure at room temperature to permit convenient handling of the gas in a vacuum line but a sufficiently low pressure at the temperature of the refrigerant to permit exposure to high vacuum.

The most popular matrix material is argon, followed by nitrogen.¹⁸ It is true, however, that other materials such as xenon and particularly krypton are often be useful.

Darling and Ogden¹⁹ in their IR study of the Pd-CO system found that, using argon, the spectra obtained were very dependent on the deposition temperature. With krypton (deposited at 15 K), however, the spectra were sharper and better resolved, and controlled diffusion studies could be carried out over a wider temperature range. Similarly, Bos and Ogden²⁰ have reported that IR spectral resolution was better in krypton than in nitrogen for their study of the Sn-O₂ system. In a study of the UV spectra of various transition-metal atoms, Schoch and Kay²¹ found superior resolution in Xe to that in Ar.

Tests of the effectiveness of different matrix materials in preventing reactions have been conducted using N₂, Ar, and Xe as the matrices.²² The active materials used were the free radical NO₂ and the compounds HBr, HCN, HN₃, NH₃, and H₂O which are capable of forming hydrogen bonds. Since NO₂ reacts to form N₂O₄, isolation of NO₂ in a matrix provides a sensitive test of the effectiveness of a matrix in preventing the diffusion and reaction of a material that is thermodynamically unstable. The use of compounds which may form hydrogen bonds also furnishes a simple method of testing the efficiency of a matrix. In general, formation of strong hydrogen bonds is accompanied by a decrease in frequency and increase in absorbance of the stretching motion of the bonded hydrogen atom and an increase in its bending frequencies. A spectrum of the material in the matrix which is similar to that of the gas is interpreted as successful isolation; a spectrum similar to that of the hydrogen bonded crystal implies failure of the matrix isolation.²²

An N₂ matrix shows better isolation of HBr, NH₃, HCN and H₂O than Ar and Xe matrices since in each case the frequencies of the molecules trapped in N₂ were closer to the gas phase than to the crystal frequencies. In the case of NO₂, an N₂ matrix gave the best isolation since NO₂ gave a sharp band very close to that of the gas phase and the

spectrum was clear in the region of absorption bands N_2O_4 band indicating that all the molecules were trapped as NO_2 rather than N_2O_4 . For HN_3 , on the other hand, Xe was the most effective matrix for the isolation at 20 K but not at 66 K. N_2 and Ar matrices appeared to isolate HN_3 molecules but the isolation was not as effective as that in Xe.

Feltrin *et al.*²³ have used Ar and N_2 as the isolating gases in the study of cerium dicarbide species. They have shown that the spectra recorded under the same conditions looked very similar except for a general and noticeable loss of intensity and sharpness of the spectral bands and the occasional absence of weak bands when Ar was used instead of N_2 . This finding is very likely due to the different polar characteristics of the two gases and led to a preferential use of N_2 gas.

IR spectra of chlorine nitrate in N_2 and Ar matrices have been studied by Griffith *et al.*²⁴ N_2 matrices were again preferred since the spectra of ClONO_2 in Ar matrices were very complex and were not simplified at higher matrix ratios probably due to complex site effects. The spectra in Ar did not show extra absorptions over those seen in N_2 matrices. Also the frequencies when N_2 was used were closer to the gas phase frequencies.

The vibrational frequencies of the monomer in a matrix may not be identical with those of the molecule in the gas phase. An increase in the dielectric constant of the medium in which the absorbing molecule is suspended generally causes a decrease in the frequency of absorption from the gas phase frequency.²⁵

1.7 Effect of Matrix Isolation on IR Spectra

In the following section some specific differences expected between IR spectra of gaseous and matrix-isolated samples are considered.

1.7.1 Matrix Effect

Typically, more absorption bands are observed in matrix isolation infrared spectra than in corresponding vapour-phase spectra. Matrix effects are primarily responsible for this observation. Matrix perturbations can induce absorptions for vibrational modes which were inactive in the vapour state.²⁶ Additional absorptions can occur because of coupling of vibrational modes with lattice (matrix) vibrations. Trapping sites in the matrix need not be identical. Slight changes in the environment of trapped species can produce absorbance band multiplicity. Absorbance bands representative of conformational isomers can be observed for some substances.^{27,28} If the ratio of matrix atoms to trapped molecules is too low, substantial interaction between trapped molecules can occur. Aggregation can produce absorbance bands characteristic of dimeric or polymeric species. Band intensities for these absorptions will be concentration dependent. The matrix behaves as a solvent for trapped molecules. As a result, matrix shifts can occur which are analogous to solvent shifts. The same factors responsible for liquid-phase solvent shifts are active for matrix shifts.²⁶ Stretching vibrations tend to shift to lower frequencies, while bending vibrations tend to shift to higher frequencies.²⁹

1.7.2 Frequency (or Matrix) Shift

The most habitual and easily identified matrix effect is the frequency shift of a spectroscopic feature relative to the value characteristic of the gas phase; this has been observed for rotational, vibrational, and electronic transitions. Vibrational frequencies are subject to matrix shifts which are usually less than 1% of the gas-phase value for

non-polar species, though shifts as large as 10% have been reported for polar molecules. Although frequencies reported for some electronic transitions may differ by as much as 4000 cm^{-1} from the gas-phase values, the frequency shifts are proportionately no greater than for vibrational transition.³⁰

For the vibrational modes of polar molecules, it has been found empirically that there is a red frequency shift; increasing the polarizability of the matrix or the charge separation of the vibrating bond tends to increase this shift. Vibrational frequencies for a range of such molecules isolated in neon and argon matrices have been represented, to a usual approximation ($\pm 6\text{ cm}^{-1}$). Less polar polyatomic molecules exhibit both positive and negative shifts of frequency.³⁰

1.7.3 Matrix Site Effect

The observation of a multiplet where only a single spectroscopic feature is anticipated is commonly attributable to variations in the matrix environment experienced by the guest. These variations may reflect (i) different orientations of the guest within a particular matrix cage, (ii) population of more than one type of cage because of the opportunities offered by substitutional, interstitial, and dislocation sites within the host lattice, and (iii) occupation of cages which include guest, as well as host, molecules as nearest or next-nearest neighbours (aggregation site effect).

1.8 Analytical Application of MI-FTIR Spectroscopy

In matrix isolation, a gaseous sample is mixed with a large excess of an inert diluent gas (the matrix) and the gaseous mixture is then deposited on an optical surface

for spectroscopic examination. Since the initial description of the technique by Whittle, Dows, and Pimentel in 1954,¹⁶ MI has seen many varied applications. The utilization of MI in the characterization of transient species has been reviewed recently^{31,32} as has the application of MI to organic chemistry.³³ The uses of MI in conjunction with FTIR spectroscopy have been discussed in many reviews.^{34,35} Recently, matrix isolation has been exploited in the design of a sensitive interface for GC/FTIR spectroscopy.³⁶⁻⁴⁰ GC/MI/FTIR spectroscopy produces infrared spectra with sharp absorption bands that are highly characteristic of molecular structure. GC/MI/FTIR spectroscopy are especially useful for distinguishing isomeric species.⁴⁰

Molecular interactions in the liquid and solid state produce significant contributions to IR absorption spectra. In contrast, molecules in a vapour or isolated in a low-temperature matrix experience minimal intermolecular interaction, because individual molecules are well separated. Therefore, vapour-phase infrared spectra should be more compatible with matrix isolation spectra than are either liquid- or solid-phase spectra. However, environmental differences between molecules in a vapour state and those trapped in a matrix can result in discrepancies in the number of absorption bands, band position, and band intensities in infrared absorption spectra.

A bibliographic survey has been done by Almond and Downs⁴¹ which provides a directory of chemical species studied by matrix isolation and reported in the period 1977 to mid-1986. The progress made in matrix-isolation spectroscopy over the period 1989 to late 1991 has been reported by Almond and Orrin.⁴² They have indicated the scope of the technique in a range of different areas and the direction which matrix-isolation is taking at the present time.

Until recently, little attention has been devoted to MI/FTIR spectroscopy as a technique for the qualitative and quantitative analysis of stable species. Rochkind⁴³⁻⁴⁶

applied MI/IR spectroscopy, using a variant of the conventional MI procedure, to analyze a mixture of gases. Using a number of compounds that are gases at room temperature, premixed with nitrogen, and pulsed deposition, Rochkind⁴⁴ demonstrated that MI/IR spectroscopy can be a more powerful qualitative tool than gas chromatography in the analysis of particular isotopic molecules. He also demonstrated the applicability of Beer's Law to matrix-isolated samples.⁴⁵

1.9 Analytical Characteristics of Matrix Isolation Spectroscopy⁴⁶

Any sample preparation technique to be used for optical spectroscopic analysis of very complex samples should exhibit as many as possible of the following characteristics:

1. The spectra of individual molecules should exhibit very narrow spectral bandwidths especially in the analysis of multicomponent samples to avoid any overlapping of spectral bands arising from different compounds and to achieve better identification and quantitation of individual substances in mixture.

2. The spectrum of an individual molecule should contain sufficient information and several distinct features for identification of that molecule but it should not be too complicated to decrease the probability of band overlap in the spectra of mixtures.

3. The spectrum of a particular compound should ideally be reproducible from one sample to the next, irrespective of wide variations in the identities and concentrations of other constituents between samples. As seen from the results presented in chapter 7 this is not always the case for complex mixtures collected in field experiments.

4. The fundamental physical constant that quantitatively relates the measured signal for a particular molecule to its concentration in the sample (i.e. the molar absorptivity for optical spectroscopy) must be independent of the amount of that compound present in the sample, and must not be altered significantly by any of the other sample constituents.

From the above criteria, it is implied that in the final spectroscopic sample, an individual molecule of an individual compound must be “unaware” of the existence of any other molecules present in the original chemical sample. In other words, the individual molecules should behave as though they are isolated from each other. It is the objective of matrix isolation spectroscopy to prepare a sample in which the individual molecules are indeed isolated, and experience only matrix host molecules as near neighbours. In matrix isolation, the sample is dispersed in the solvent (the matrix) in the vapour phase. The actual spectroscopic sample is a cryogenic solid, in which it is intended that the molecular randomness characteristic of a gaseous sample be maintained. It is desired to perform the spectroscopic analysis in a low-temperature solid, in order to minimize the bandwidths of individual spectral lines and to remove rotational fine structure from the spectrum. It is obvious that the technique as described above is applicable only to vapour-phase samples, and to liquid and solid samples which can be vapourized without degradation. Any sample amenable to analysis by gas chromatography or mass spectrometry can in principle be analyzed by matrix isolation spectroscopy.

1.10 Instrumentation

The basic components of a system for the preparation of matrix-isolated samples of liquid or solid analytes are: (1) a cell, which is used to vaporize the sample; (2) a refrigerator, equipped with a suitable substrate onto which the matrix isolated sample can be deposited; and (3) a vacuum line to control the deposition process.

1.11 This Work

In the present work the advantages of matrix isolation are combined with the use of relatively simple apparatus by using the natural atmospheric CO₂ as the matrix host material at temperatures of 77 K or lower and all trace gas absorptions may be measured relative to CO₂ absorptions. Previously the small number of matrix isolation experiments carried out in the area of atmospheric gas analysis have utilised rather complex apparatus involving liquid helium or closed cycle helium gas refrigerators. It is hoped that the apparatus used in the current work will prove to be more straightforward to use and more amenable to field studies.

1.12 Objectives

The main objectives of this research are (i) to develop the matrix isolation method to be used in field work by using a simple liquid-nitrogen-cooled Dewar to condense samples; (ii) to trap atmospheric pollutants in CO₂ at 77 K, and (iii) to measure IR spectra for the sample mixtures and to obtain the concentrations of these pollutants in these samples. The sampling procedure is mainly based on passing the air

sample through a trap held at 77 K. Thus the CO₂, H₂O and the condensable pollutants are fractionated from the sample. Water may be removed by passing through a second trap held at ca. -40°C. The gaseous mixture of CO₂ and condensable pollutants is then sprayed onto a pre-cooled spectroscopic window held at 77 K. The IR spectra are then measured and the ratio of pollutant to CO₂ are calculated. Calibration curves must first be constructed for different pollutants based on the ratio of pollutant peak area to CO₂ peak area.

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Chapter 2 Theory Behind Vibrational Spectroscopy

2.1 Dipole Change During Vibrations and Rotations

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these circumstances can the alternating electrical field of the radiation interact with the molecule and cause a change in the amplitude of one of its motions. For example, the charge distribution around a molecule such as hydrogen chloride is not symmetric, because the chlorine has a higher electron density than the hydrogen. Thus, hydrogen chloride has a significant dipole moment and is said to be polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centres of charge. As a hydrogen chloride molecule vibrates, a regular fluctuation in dipole moment occurs, and a field is established that can interact with the electrical field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of the molecule, a net transfer of energy takes place that results in a change in the amplitude of the molecular vibration; absorption of radiation is the consequence. Similarly, the rotation of asymmetric molecules around their centres of mass results in a periodic dipole fluctuation that can interact with radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear species such as O_2 , N_2 or Cl_2 ; consequently, such compounds cannot absorb in the infrared.

2.2 Vibration-Rotation Spectroscopy

There is a stack of rotational energy levels associated with all vibrational levels.

In rotational spectroscopy transitions occur between rotational energy levels associated with the same vibrational level. In vibration-rotation spectroscopy, transitions occur between stacks of rotational energy levels associated with two different vibrational levels. These transitions accompany all vibrational transitions but the rotational transitions are most usually observed normally in the gas phase at low pressure.

The energy required to cause a change in rotational level is minute and corresponds to radiation of 100 cm^{-1} or smaller. Because rotational levels are quantized, absorption by gases in this far-infrared region is characterized by discrete, well-defined lines. In liquids or solids, intramolecular collisions and interactions cause broadening of the lines into a continuum. Vibrational energy levels are also quantized, and for most molecules the energy differences between the quantum vibrational states correspond to the mid-infrared region. The infrared spectrum of a gas usually consists of a series of closely spaced lines, because there are several rotational energy states for each vibrational state. On the other hand, rotation is highly restricted in liquids and solids; in such samples, discrete vibrational/rotational lines disappear, leaving only somewhat broadened vibrational peaks. Likewise for matrix-isolated samples, for all but the smallest molecules, no rotational motion is possible within the matrix so no rotational fine structure is observed.

2.3 Types of Molecular Vibrations

The relative positions of atoms in a molecule are not exactly fixed but instead fluctuate continuously as a consequence of a multitude of different types of vibrations. For a simple diatomic or triatomic molecule, it is easy to define the number and nature of such vibrations and relate these to energies of absorption. An analysis of this kind

becomes difficult if not impossible for molecules that have a large number of vibrating centres; here interactions among several centres can occur and must be taken into account.

Vibrations fall into the basic categories of stretching and bending. A stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms. Bending vibrations are characterized by a change in the angle between two bonds and are of four types: scissoring, rocking, wagging, and twisting. The various types of vibrations are shown schematically in Figure 2.1.

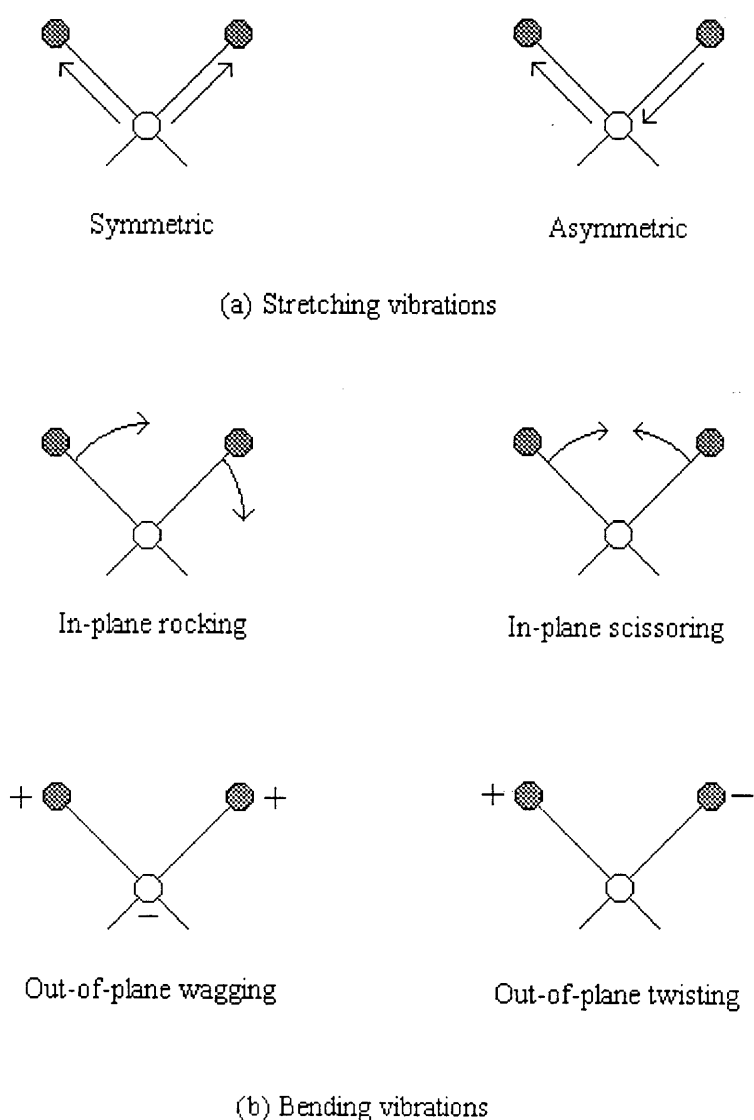


Figure 2.1 Types of molecular vibrations. Note: + indicates motion from the page toward the reader; - indicates motion away from the reader.

All of the vibration types shown in Figure 2.1 may be possible in a molecule containing more than two atoms. In addition, interaction or coupling of vibrations can occur if the vibrations involve bonds to a single central atom. The result of coupling is a change in the characteristics of the vibrations involved.

2.4 Diatomic Molecules

The classical analogy of a vibrating diatomic molecule is that of two weights connected by a spring. The potential energy of such a vibrating system is related to the displacement of the weights relative to each other along the axis of the spring. If the motion is *simple harmonic* the relation is given by $E = \frac{1}{2}fx^2$ where E denotes potential energy, x the displacement and f the force constant or stiffness of the spring. The equation describes a parabola and shows that identical changes in potential energy occur on stretching or compressing the spring. A diatomic molecule behaves rather differently in that the forces of internuclear repulsion arising when the bond is compressed build up rapidly, whilst, on stretching, the bond weakens and may finally break. The resulting vibrational motion is *anharmonic* in nature and the mathematical relation between potential energy and displacement is more complex.

The concept of discrete or quantized energy levels can be superimposed on this diagram by representing them as a series of horizontal lines, the spacing of which becomes closer with increasing energy due to the anharmonic nature of the vibration. In quantum mechanical terms, these levels are labelled $v = 0, 1, 2, 3 \dots$, where v is the vibrational quantum number, and the general mathematical expression for the potential energy of the system expressed in wavenumbers is given by

$$\epsilon_{\text{vib}} = (v + \frac{1}{2}) \sigma_e - (v + \frac{1}{2})^2 \sigma_e \chi_e \text{ cm}^{-1} \quad 2.1$$

σ_e denoting the equilibrium vibration frequency and χ_e the anharmonicity constant. This expression may be used to predict the appearance of the absorption spectrum of a diatomic molecule. At room temperature most molecules are in the ground vibrational state ($v = 0$) so that only transitions from this level need to be considered. Although basically a simple spectrum simultaneous rotational transitions produce a pattern of fine structure lines on either side of the vibrational transition. Rotational fine structure is not usually resolved for samples run in the liquid state or in solution. This is due to collisional broadening and the resulting spectrum would have the appearance shown in Figure 2.2. For a given molecule, and using the classical analogy considered earlier, the

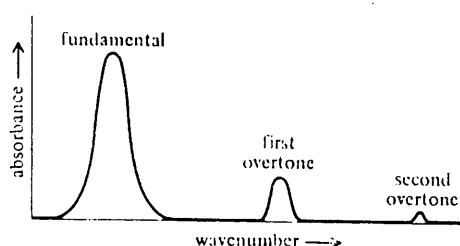


Figure 2.2 Infrared spectrum of a diatomic molecule in solution

positions of the fundamental and hence the overtone, are determined by the atomic masses m_1 and m_2 , and the stiffness, or force constant, of the bond. These are related by the equation

$$\sigma_e = \frac{1}{2}\pi c (f/\mu)^{1/2} \quad 2.2$$

where f is the force constant of the bond and μ the reduced mass, given by $(m_1 m_2)/(m_1 + m_2)$.

2.5 The Harmonic Oscillator

Isolated vibrations may be considered by employing a simple mechanical model called the harmonic oscillator. The characteristics of an atomic stretching vibration can be approximated by a model consisting of two masses connected by a spring. A disturbance of one of these masses along the axis of the spring results in a vibration called simple harmonic motion.

Let us first consider the vibration of a single mass attached to a spring that is hung from an immovable object (Figure 2.3). If the mass is displaced a distance q from its equilibrium position by application of a force along the axis of the spring, the restoring force f is proportional to the displacement (Hooke's law). That is

$$f = -kq \quad 2.3$$

where k is the force constant.

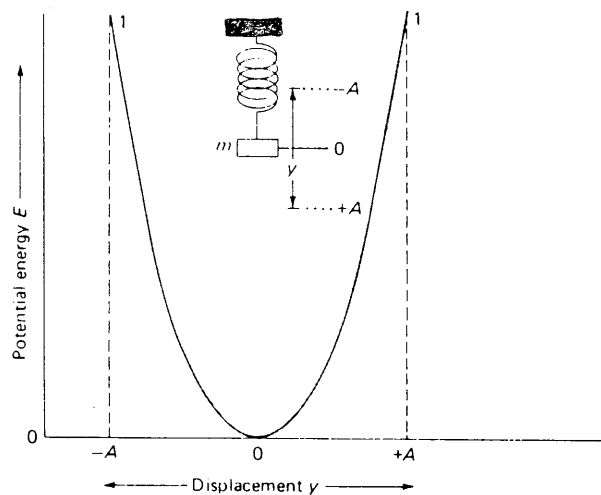


Figure 2.3 Potential energy diagram showing the vibration of a single mass; an oscillator which obeys Hooke's Law is said to be a Harmonic Oscillator.

The potential energy E of the mass and spring can be considered to be zero when the mass is in its rest or equilibrium position. As the spring is compressed or stretched, however, the potential energy of this system increases by an amount equal to the work required to displace the mass. If the mass is moved from some position q to $(q+dq)$, the work and hence the change in potential energy dE are equal to the force f times the distance dq . Thus

$$dE = -fdq \quad 2-4$$

Combining Equations 2-3 and 2-4 yields

$$dE = kq dq \quad 2-5$$

Integrating between the equilibrium position ($y = 0$) and y gives

$$E = \frac{1}{2}kq^2 \quad 2-6$$

The potential-energy curve for a simple harmonic oscillation, derived from Equation 2.6, is a parabola as in Figure 2.4. The potential energy is a maximum when the spring is stretched or compressed to its maximum amplitude A , and decreases to zero at the equilibrium position.

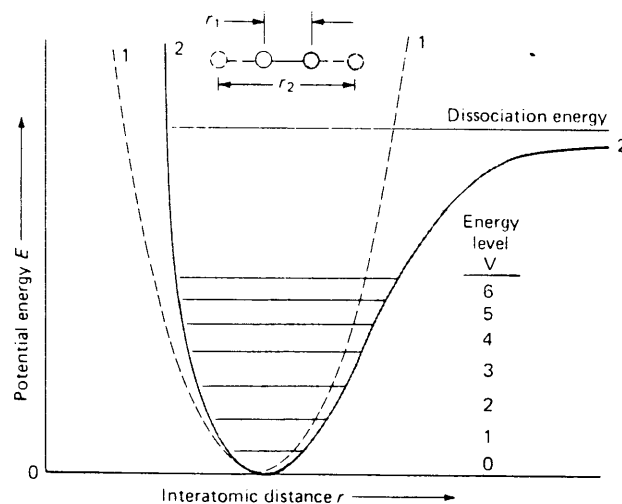


Figure 2.4 Potential energy diagram. Curve 1, harmonic oscillator. Curve 2, anharmonic oscillator.

2.6 The Anharmonic Oscillator

The parabolic potential well in Figure 2.4 (curve 1) is actually a pretty poor representation of the force felt by diatomic molecules. A real molecule ought to have an asymmetric potential well. The potential energy of such a vibrator changes periodically as the distance between the masses fluctuates. For example, as the two atoms approach one another, repulsion between the two nuclei produces a force that acts in the same direction as the restoring force of the bond. This repulsion grows very strong at small values of q ; thus the potential energy can be expected to rise more rapidly than the harmonic approximation predicts. On the other hand, as q gets bigger the restoring force, and thus the potential energy, eventually levels off and the molecule dissociates. Such a potential well is shown in Figure 2.4 (curve 2).

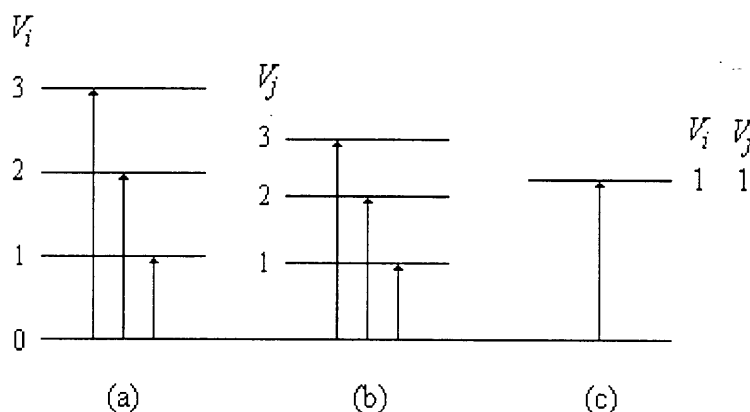


Figure 2.5 (a, b) Fundamental and overtone, and (c) combination transitions involving vibrations ν_i and ν_j .

Anharmonicity leads to deviations of two kinds. At higher quantum numbers, ΔE becomes smaller (see curve 2 in Figure 2.4), and the selection rule that Δv should be ± 1 is not rigorously followed; as a result transitions of $\Delta v = \pm 2$ or ± 3 are observed. Such transitions are responsible for the appearance of overtone lines at frequencies

approximately two or three times that of the fundamental lines; the intensity of overtone absorption is frequently low, and the peaks may not be observed. Vibrational spectra are further complicated by the fact that two different vibrations in a molecule can interact to give absorption peaks with frequencies that are approximately the sums or differences of their fundamental frequencies (Figure 2.5). Again, the intensities of combination and difference peaks are generally low.

2.7 Selection Rules and Polarization

The selection rules tell us which transitions we might hope to see in the spectrum. In a real spectrum we find band intensities varying from very weak to very strong. The selection rules do not predict how intense a band will be. They merely tell us which transitions are expected to have zero intensity and which have nonzero intensity. Transitions predicted to have zero intensity are said to be *forbidden* and those predicted to have nonzero intensity are said to be *allowed*. Transitions predicted to be observed in the IR spectrum are called *infrared active* while those expected in the Raman spectrum are *Raman active*. Depending on the symmetry of the molecule, some transitions may appear in one or the other spectrum, or both, or neither. A vibration transition is IR active if the dipole moment of the molecule changes during the vibration. Of the two vibrations of ethylene in Figure 2.6, the totally symmetric mode does not change the dipole moment and will not be IR active. The asymmetric stretch does change the dipole moment and will be IR active. A more thorough treatment of the vibrational spectrum of ethylene is given later in this chapter.

The IR selection rules for diatomic molecules states that in a transition from the state v to the state v' the only allowable changes in the quantum numbers are $\Delta v = \pm 1$.

However, as mentioned previously this selection rule breaks down as a result of anharmonicity and overtone bands resulting from vibrational transitions with $\Delta v = \pm 2$, ± 3 , etc. may be observed.

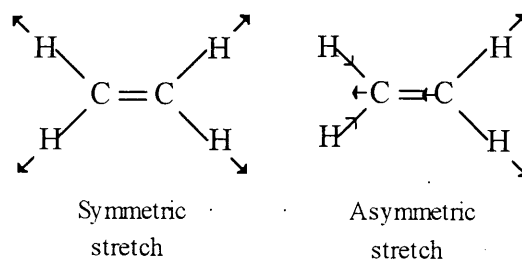


Figure 2.6 Stretching vibrations of ethylene.

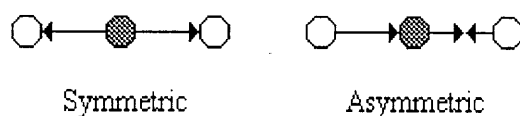
2.8 Vibrational Coupling

The energy of a vibration, And thus the wavelength of its absorption peak, may be influenced (or coupled) by other vibrations in the molecule. A number of factors that influence the extent of such coupling can be identified.

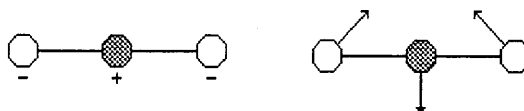
1. Strong coupling between stretching vibrations occurs only when there is an atom common to the two vibrations.
2. Interaction between bending vibrations requires a common bond between the vibrating groups.
3. Coupling between a stretching and a bending vibration can occur if the stretching bond forms one side of the angle that varies in the bending vibration.
4. Interaction is greatest when the coupled groups have individual energies that are approximately equal.
5. Little or no interaction is observed between groups separated by two or more bonds.

6. Coupling requires that the vibrations be of the same symmetry class.

The infrared spectrum of carbon dioxide can be used as a good example of coupling effects. If no coupling occurred between the two C=O bonds, an absorption peak would be expected at the same wavenumber as the peak for the C=O stretching vibration in an aliphatic ketone (about 1700 cm^{-1}). Experimentally, carbon dioxide exhibits two absorption peaks, the one at 2330 cm^{-1} and the other at 667 cm^{-1} . Carbon dioxide is a linear molecule and thus has four normal modes ($3 \times 3 - 5$). Two stretching vibrations are possible. In principle interaction between the two vibrations could occur because the bonds involved are associated with a common carbon atom. However, one of the coupled vibrations is symmetric and the other is asymmetric, so they belong to different symmetry classes implying that there will, in fact, be little or no coupling.



The symmetric vibration (ν_1) causes no change in dipole, because the two oxygen atoms simultaneously move away from or toward the central carbon atom. Thus, the symmetric vibration is infrared inactive. In the asymmetric vibration (ν_2), one oxygen moves away from the carbon atom as the carbon atom moves toward the other oxygen. As a consequence, a net change in charge distribution occurs and absorption at 2330 cm^{-1} results. The remaining two vibrational modes of carbon dioxide involve scissoring, as shown below.



These two bending vibrations are the resolved components of the bending motion in all possible planes around the bond axis. The two vibrations (ν_3) are identical in energy (degenerate) and thus produce one peak at 667 cm^{-1} .

It is of interest to compare the spectrum of carbon dioxide with that of nonlinear, triatomic molecules such as water, sulfur dioxide, or nitrogen dioxide. These molecules have $(3 \times 3 - 6)$, or 3, vibrational modes which take the following forms. Because the central atom is not in line with the other two, a symmetric stretching vibration will produce a change in dipole and will thus be responsible for infrared absorption. For example, stretching peaks at 3650 and 3760 cm^{-1} are observed for the symmetric and asymmetric vibrations of the water molecule. Only one scissoring vibration exists for this nonlinear molecule, because motion in the plane of the molecule constitutes a rotational degree of freedom. For water, the bending vibration causes absorption at 1595 cm^{-1} . The difference in behaviour of linear and nonlinear triatomic molecules (two and three absorption peaks, respectively) illustrates how infrared absorption spectroscopy can sometimes be used to deduce molecular shapes.

Coupling of vibrations is a common phenomenon; as a result, the position of an absorption peak corresponding to a given organic functional group cannot be specified exactly. For example, the C-O stretching frequency in methanol is 1034 cm^{-1} , in ethanol it is 1053 cm^{-1} and in 2-butanol it is 1105 cm^{-1} . These vibrations result from a coupling of the C-O stretching with adjacent C-C stretching or C-H vibrations.

2.9 Group Vibrations

As mentioned previously an N -atomic non-linear molecule has $3N-6$ normal modes of vibration. This follows from each atom having three degrees of freedom due to the need to specify three coordinates, x , y , and z , to define the position of each. Of the total of $3N$ degrees of freedom for the molecule, three represent the translation of the molecule as a whole along x , y , or z axis and another three represent rotation of the molecule about each of these axes. The remaining $3N-6$ degrees of freedom represent motions of the nuclei relative to each other, namely the vibrations. For a linear molecule there are $3N-5$ normal modes of vibration because there is no degree of freedom corresponding to rotation about the internuclear axis.

2.10 Polyatomic Molecules

For polyatomic molecules, whose spectra are usually recorded as liquids, solid or in solution, the complexity of the spectrum increases rapidly with the number of atoms N in the molecule, because, number of fundamentals, or *normal modes* of vibration is given by $3N-6$ and $3N-5$ for bent and linear molecules respectively (see Figure 2.7). A *normal mode* of vibration is defined as the movement of all the atoms of the molecule in phase. In the case of polyatomics, the number of fundamentals includes both stretching and bending vibrations, the latter involving changes of bond angle. There are associated overtones with each fundamental and, in addition, other absorption bands may arise due to interactions between certain of the fundamentals and overtones. These are known as *combination* and *Fermi resonance* bands. The overall appearance of the spectrum is that of a large number of resolved and partially resolved bands of

varying intensity. The most intense bands are fundamentals in which there is a large change of dipole moment during the vibration. Conversely, a band may be weak or absent if the dipole change is small or zero. Many bands can be assigned to the vibration of particular chemical groups within a molecule, the wavenumber being largely independent of the rest of the structure. Such *characteristic vibration frequencies* are of paramount importance in obtaining structural information and in the identification of unknown compounds.

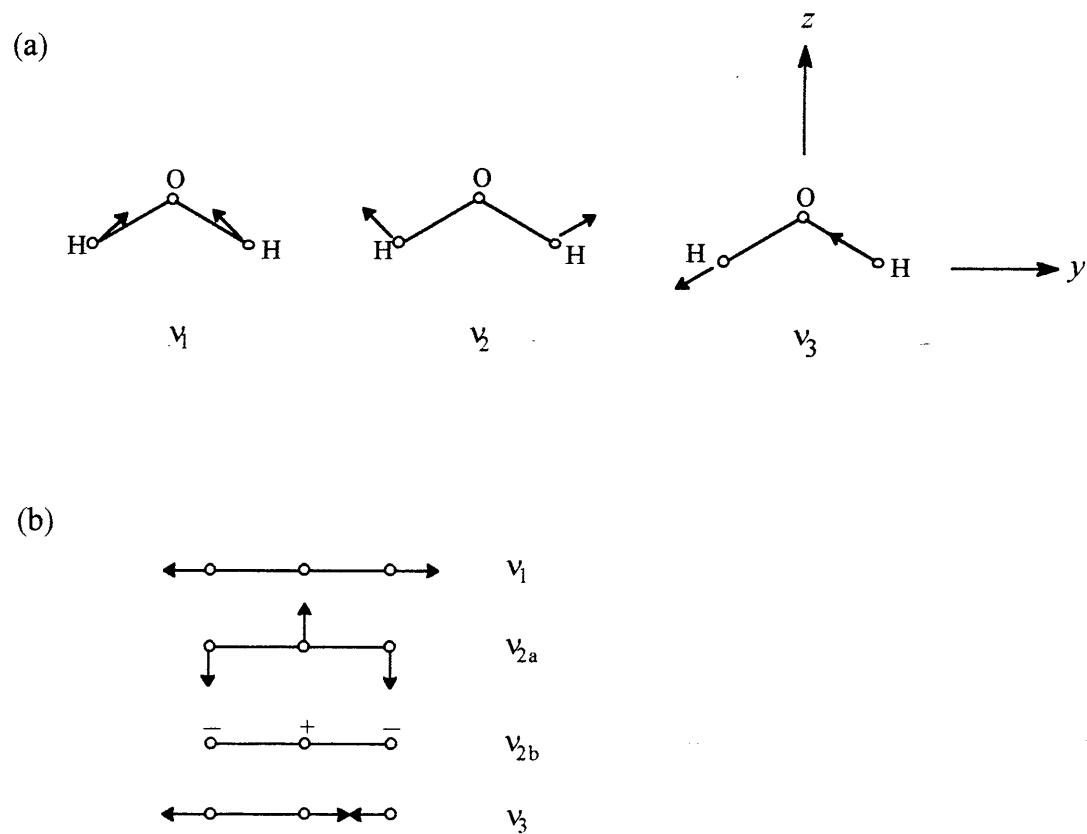


Figure 2.7 The normal vibrations of H_2O (a) and CO_2 (b) molecules.

2.11 Characteristic Vibration Frequencies

The occurrence of characteristic vibration or group frequencies can be explained in terms of relative masses and force constants using the classical analogy of weights and springs as shown in Figure 2.8.

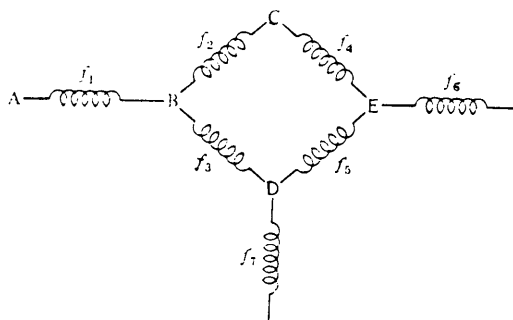


Figure 2.8 Classical analogy of a polyatomic molecule.

2.11.1 Mass Effect

If the masses $A, B, C, \dots$ are all similar and the force constants $f_1, f_2, f_3, \dots$ are of the same magnitude, the vibrations of individual atoms are strongly coupled with the result that no band can be assigned solely to any particular group of atoms. If, however, the mass of atom A is considerably smaller than those of the other atoms, one mode of vibration will involve the stretching of the bond between A and the rest of the molecule. The system can be considered as approximating to a diatomic molecule $A-X$.

2.11.2 Force Constant Effect

Considering the same model as that shown in Figure 2.8, if the force constant of the $A-B$ bond is significantly higher than those for the rest of the molecule, one

stretching vibration will occur at higher wavenumber as the equilibrium vibration frequency σ_e is directly proportional to f_{A-B} . This situation arises in molecules with unsaturated groups such as C=C, C $\equiv$ C and C=O because the magnitude of the force constant increases significantly with bond order.

2.12 Factors Affecting Group Frequency

2.12.1 Hydrogen Bonding

Compounds containing proton donor groups such as O-H and N-H can be involved in intra- or intermolecular hydrogen bonding in the presence of proton acceptors, e.g. O, N, halogen, or C=C. The stiffness of the X-H bond is thereby lessened resulting in a lowering of the stretching frequency, and the band broadens and often intensifies. Conversely, the frequency of the bending mode is raised but the effect is much less pronounced. *Intermolecular* hydrogen bonding is suppressed at elevated temperatures but it is favoured by a high solute concentration. *Intramolecular* hydrogen bonding is also reduced at elevated temperatures but it is unaffected by changes in solute concentration. These effects are particularly significant in the spectra of alcohols, phenols, carboxylic acids and amines.

2.12.2 Adjacent Groups

The wealth of structural information that can be obtained from infrared spectra arises largely from differences in band position, shape and intensity that are observed when comparing similar but not identical compounds. Predictable shifts occur on

altering the substituents or structure adjacent to a group giving rise to a particular absorption. These can be explained in terms of an *inductive effect*, a *resonance effect* and *steric factors* such as ring strain. The effects are represented by the carbonyl group, whose stretching frequency occurs within the range 1650 to 1850 cm^{-1} . Shifts are usually related to the position of the carbonyl band in pure acetone (1715 cm^{-1}). The proximity of electron withdrawing substituents causes an inductive withdrawal of electron density from around the oxygen atom thereby shortening the bond (Figure 2.9). This increases the force constant and hence the wavenumber of the vibration. If the adjacent group contains a weakly electronegative atom with lone-pair electrons or electrons occupying π -orbitals, resonance interaction with electrons in the carbonyl group leads to a reduction in bond order (Figure 2.9). The corresponding smaller force constant results in a lower value for the wavenumber of the vibration. Steric hindrance may inhibit the resonance effect by reducing the coplanarity of a conjugated system whilst carbonyl groups which form part of a strained ring system absorb at high wavenumbers because of the constraint imposed upon the carbon atom.

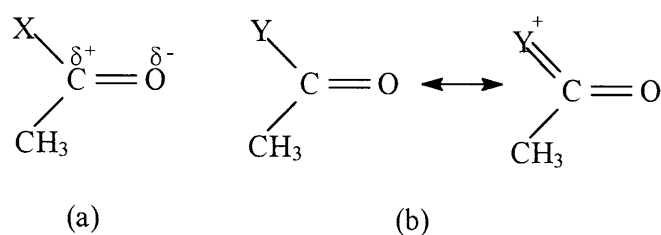


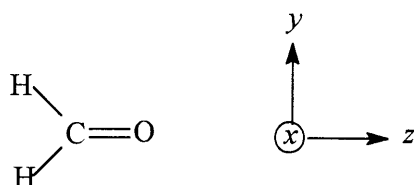
Figure 2.9 Effect of substitutions on the carbonyl bond. (a) Inductive effect, X = H, OH, OR, halogen. (b) Resonance effect, Y = NH_2 , NHR, NR_2 , phenyl.

2.13 The infrared active fundamentals

It is apparent that some vibrations of symmetric molecules, such as the asymmetric stretching of CO_2 , i.e., $\leftarrow \text{O}=\text{C}=\text{O} \rightarrow$, have no oscillating dipole moment and

therefore cannot interact with electromagnetic radiation. Furthermore, the necessarily zero oscillating dipole moment is a result of the symmetry of the molecule and the symmetry type of the vibration. It is possible to decide for which symmetry types the fundamental transition will be active, i.e., for which symmetry type the oscillating dipole moment will not necessarily be zero.

This can be done using group theory; two examples of molecules whose spectra are discussed later in the thesis are taken here as examples. These are formaldehyde and ethylene. Formaldehyde belongs to the C_{2v} point group which has the symmetry elements I , C_2 , $\sigma_v(xz)$ and $\sigma'_v(yz)$. The axis convention used for this molecule follows the Mulliken recommendation⁵ and is depicted below.



The representation of the C-H vectors is as follows.

C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
(C-H)	2	0	0	2

The number of times each irreducible representation appears in this representation is obtained from the expression:

$$\frac{1}{h} \sum_R \chi_i(R) \chi_{rr}(R)$$

The order of the group (h) is 4 here, and the reduction gives:

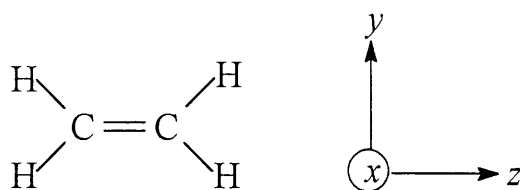
$$\Gamma_{(C-H)} = A_1 + B_2$$

From the character table

C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	T_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	1	1	-1	-1	R_z	α_{xy}
B_1	1	-1	1	-1	T_x, R_y	α_{xz}
B_2	1	-1	-1	1	T_y, R_x	α_{yz}

We see that A_1 transforms as z and B_2 as y so we expect two $\nu(\text{C-H})$ bands in the infrared spectrum of A_1 and B_2 symmetry. For Raman activity we look to the quadratic functions and here the behaviour is $A_1 (x^2, y^2, z^2)$, $B_2 (yz)$ so we also expect these two $\nu(\text{C-H})$ vibrations to be Raman active.

Ethylene belongs to the D_{2h} point group which has the symmetry elements I , $C_2(z)$, $C_2(y)$, $C_2(x)$, i , $\sigma(xy)$, $\sigma(xz)$ and $\sigma(yz)$. Clearly it is of importance here to state the axis convention being used. The one used here follows the Mulliken recommendation and is shown below.



The z axis is taken as the $\text{C}=\text{C}$ axis while the x axis is perpendicular to the plane of the molecule. The representation of the C-H vectors is as follows:

D_{2h}	I	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
(C-H)	4	0	0	0	0	0	0	4

The order of the group (h) is 8 here, and the reduction gives:

$$\Gamma_{(\text{C-H})} = A_g + B_{3g} + B_{1u} + B_{2u}$$

From the character table:

D_{2h}	1	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, α_{xy}
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, α_{xz}
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, α_{yz}
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x

it can be seen that A_g transforms as x^2, y^2, z^2 , B_{3g} as yz , B_{1u} as z and B_{3u} as x . We therefore expect two IR active $\nu(\text{C-H})$ vibrations of B_{3g} and B_{1u} symmetry and two Raman active $\nu(\text{C-H})$ vibrations of A_g and B_{3g} symmetry. As expected for a centrosymmetric molecule there is no coincidence between the IR and Raman bands.

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4. Harris, D. C. and Bertolucci, M. D. *Symmetry and Spectroscopy (An Introduction to Vibrational and Electron Spectroscopy)*, 1978, Dover Publications, New York.
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Chapter 3 Experimental Procedures

3.1 Vacuum Line

A simple vacuum line such as that pictured in Figure 3.1 is adequate for the mixing and deposition processes. It is an all glass variety fitted with Young's taps. The pumping system comprised a glass mercury diffusion pump backed by a Speedivac high vacuum rotary pump. A pressure of *ca.* 1×10^{-4} mmHg was thus attainable. A mercury manometer built into the line was used to measure pressures. Any leakage of air into the line was detected using a Tesla coil.

3.2 Calibration of the Vacuum Line

The vacuum line was calibrated to calculate the volume between each pair of taps as follows:

1. The vacuum line was pumped out and a bulb of a known volume was filled with air at the atmospheric pressure and connected to the line at position 22.
2. All the taps were closed (except the manometer tap) and the pressure was measured at this point as the initial pressure.
3. The bulb tap was opened and the manometer reading was taken.
4. One tap at a time was opened and the manometer reading was taken after each step.
5. The volume of each part of the line was determined using the ideal gas equation; i.e. $(P_1 V_1 = P_2 V_2)$.

The calibration procedure was repeated to get accurate measurements. The results of the line calibration is shown in Table 3.1.

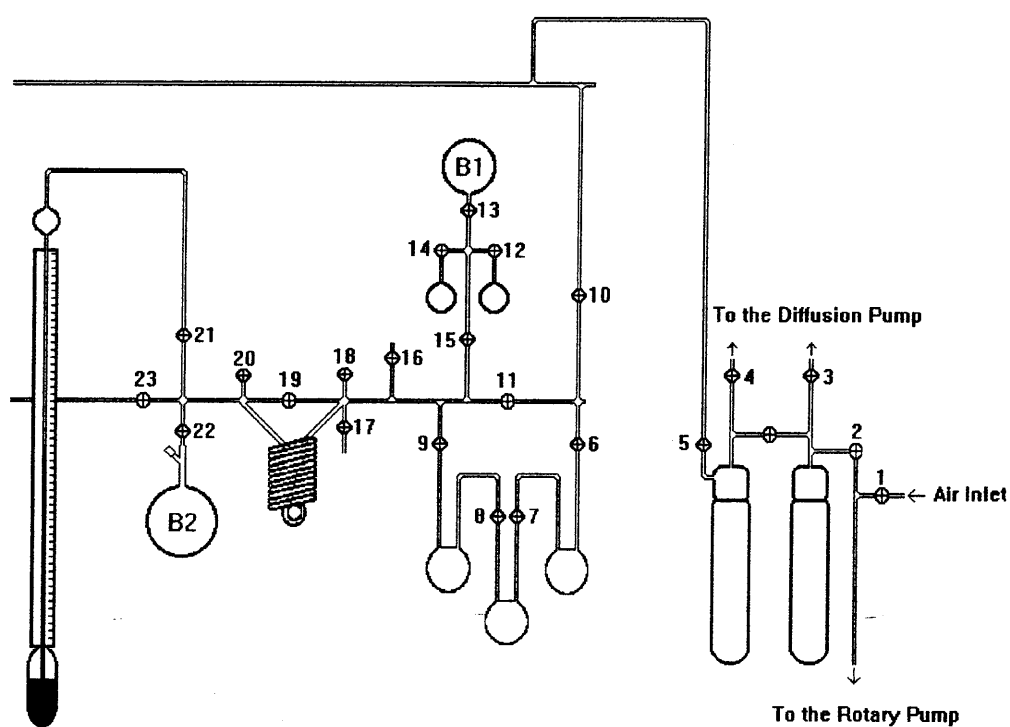


Figure 3.1 The main vacuum line used for gas mixture preparation and deposition

Table 3.1 Calibration of the Vacuum Line:

<u>Tap #</u>	<u>Calibration 1</u> <u>(vol. cm³)</u>	<u>Calibration 2</u> <u>(vol. cm³)</u>	<u>Calibration 3</u> <u>(vol. cm³)</u>	<u>Average</u> <u>volume^a</u>
22	137.6	130.6	132.2	133.5
20	74.1	77.4	75.3	75.6
19	37.0	46.9	40.1	41.3
18	0.0	0.0	0.0	0.0
11	22.3	24.7	27.8	24.9
9	32.8	35.3	33.8	34.0
8	29.3	35.8	36.7	33.9
7	30.4	32.4	33.4	32.1
6	0.0	0.0	0.0	0.0
15	10.7	6.7	10.6	9.3
14	112.9	118.3	119.1	116.8
13	1078.2	1052.8	1067.8	1066.3
12	58.1	58.8	57.7	58.2
Total	1623.4	1619.7	1634.5	1625.9

^a Approximate error limits $\pm 5\%$

3.3 Cryogenic Equipment

Measurements to liquid nitrogen temperature may be carried out with a cell such as that shown in Figure 3.2. This is a direct transmission type cell that can conveniently be inserted into the beam of the infra-red spectrometer without changing the optical path. The cell is composed of a copper cooling block, a coolant reservoir, and an enveloping jacket. The inner Pyrex tube is the container for the liquid nitrogen and is attached to a copper window holder with a copper to glass seal. Both the outer cryostat windows and the inner refrigerated window are made from CsI. The cell employed a rotatable cooled window which could be brought normal to the spray-on nozzle, the spectrometer beam and the photolysing radiation in turn (Figure 3.3). The space between the sample cell and the external windows was evacuated to provide insulation and avoid condensation of water vapour on the cool windows. The sample is cooled by

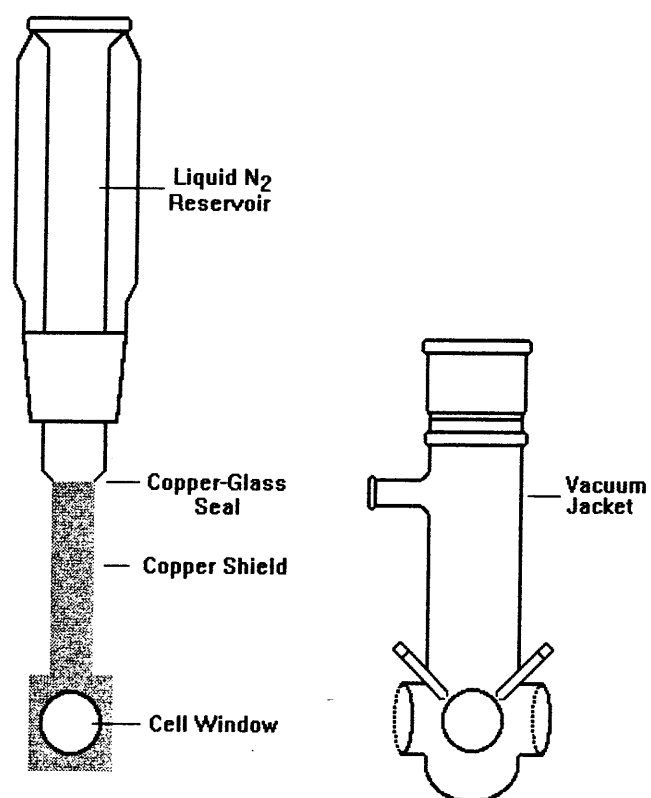


Figure 3.2 The cold cell used for sample deposition.

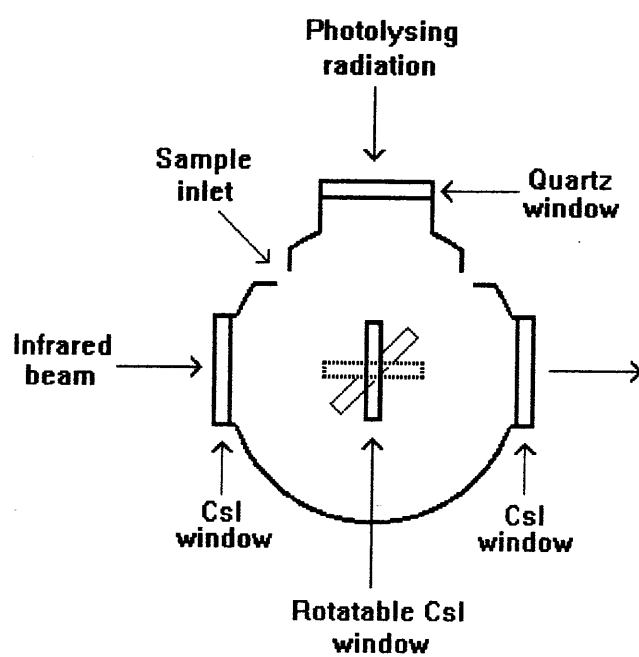


Figure 3.3 Schematic plan of a matrix isolation assembly suitable for IR measurements and for photolysis experiments.

conduction through the glass-to-metal seal which is in good thermal contact with the glass reservoir holding the coolant. All matrix depositions were performed at 77 K.

3.4 Sources of Reagents

In all of the following procedures, dry ice was used as a source of CO₂ gas. N₂O (99%, Aldrich), SO₂ (99.9%, Fluka) and ethylene (99.7%, Argo) were used directly from lecture bottles. Liquid acetone (99.5%), acetaldehyde (99%), acetic acid (99.8%) and formic acid (98%) were obtained from BDH and were used without further purification. Liquid chloroform (99%), ethyl acetate (99%) and carbon tetrachloride (99%) were obtained from BDH and were used without further purification for the preparation of “slush baths”. The materials used as adsorbents were charcoal (decolourizing powder, activated BDH), alumina (Merck), kieselguhr (calcinated DAB, purum, Fluka) and molecular sieve Type 5A (aluminium calcium silicate, 1/8” pellets, BDH).

3.5 Preparation of Gas Mixtures

Bulb B₁ (Figure 3.1) was filled with CO₂ gas to be used for preparing the gas mixtures as follows. The vacuum line including bulb B₁ was evacuated and then pressurised with CO₂ gas using dry ice as the source of CO₂. After introducing about 500 Torr of CO₂ gas bulb B₁ was closed and the line was re-evacuated. The majority of the experiments were performed using total pressures of 100 Torr and above, and in these cases the procedure for making up a gas mixture is described below.

3.5.1 Acetone/CO₂ Mixtures

Before preparing acetone/CO₂ mixtures, an ampoule half-filled with acetone was connected to the line and a Dewar filled with liquid nitrogen was placed around it to freeze the acetone. After about 30 minutes, the air above the frozen acetone was pumped out. The acetone container was closed and the acetone was warmed to melt and to get any dissolved air out of it. It was frozen again and the procedure was repeated to get rid of all dissolved air. This “freeze-pump-thaw” procedure was followed before preparing all sample mixtures when the reagent used is liquid.

Liquid nitrogen is a convenient and inexpensive refrigerant but a wider range of low-temperature baths is necessary for trap-to-trap fractionation of gases and for the characterisation of a substance by vapour pressure measurements. A convenient constant-temperature slush bath consists of a mixture of frozen compound in equilibrium with its liquid. For gas mixtures including acetone, a slush bath was prepared to get a low temperature at which acetone has a known vapour pressure. The chosen slush bath was one formed from chloroform and liquid nitrogen which gives a temperature of -63.5°C. This slush bath was chosen since acetone has a vapour pressure of 1 Torr at -59.4°C. The bath was prepared by the following method:¹

A clean Dewar was three-quarters filled with pure chloroform and placed in the fume hood. Freshly drawn liquid nitrogen was slowly added while the liquid was rapidly stirred with a stirring rod. The consistency of the final product was similar to a thick malt. It had a temperature of -61.4°C.

The slush bath was placed around the ampoule containing acetone at position 22 on the line and the receiver flask (in which the mixture was to be prepared) was connected at position 17. The ampoule containing acetone was left in the bath for about

30 minutes to reach thermal equilibrium. T11 and T15 were closed. The acetone container and the receiver flask were opened to collect acetone at this low pressure. After the low pressure of acetone had been shared into the mixing bulb (B₂) the ampoule containing liquid acetone and the mixing bulb were closed and the line was pumped out. CO₂ gas was introduced to the line and the pressure change was recorded using the manometer. The mixing bulb was opened to mix the two gases and the new pressure was recorded. Different amounts of CO₂ were used to prepare mixtures of different concentrations. The presence of small pieces of Teflon in the mixing bulb facilitated efficient mixing (see Section 3.5.5).

3.5.2 Acetaldehyde/CO₂ Mixtures

An ethyl acetate slush bath has a temperature of -83.6°C and it was chosen for experiments in which mixtures containing acetaldehyde were made up since acetaldehyde has a vapour pressure of 1 Torr at -81.5°C. All the above procedure was repeated to prepare acetaldehyde/CO₂ mixtures.

3.5.3 Formic Acid/CO₂ Mixtures

A carbon tetrachloride slush bath with a temperature of -22.7°C was used for these experiments since formic acid has a vapour pressure of 1 Torr at -20.0°C. Mixtures of different concentrations of formic acid in CO₂ were prepared. In a separate series of experiments different pressures of water vapour were added to mixtures of 6% formic acid in CO₂ in order to probe the effect of water upon the spectrum of formic acid isolated in CO₂ matrices. It was thought possible that water could have a relatively

large effect upon the infrared spectrum of formic acid since hydrogen bonding between these two reagents is possible.

3.5.4 Acetic Acid/CO₂ Mixtures

A carbon tetrachloride slush bath was used in preparing the mixtures since acetic acid has a vapour pressure of 1 Torr at -17.2°C. Mixtures of different concentrations of acetic acid in CO₂ were prepared.

3.5.5 N₂O/CO₂ Mixtures

A dilute mixture (usually 1 part in 10) of N₂O in CO₂ was first prepared. A 100 mL external bulb (B₂) was evacuated and then pressurised with a measured amount of N₂O obtained directly from the lecture bottle. The pressure was measured on the manometer. The rest of the line was then re-evacuated and pressurised with CO₂ gas from the CO₂ storage bulb (B₁). The tap of the external bulb was then opened to allow mixing of the two gases. The pressure change was then recorded to obtain the concentration of N₂O in CO₂. In order not to lose any N₂O it was necessary to fill the line with CO₂ to a pressure greater than that in the external bulb. The tap of this bulb was then opened and closed quickly to admit some CO₂. The line was then pressurised a little more and the operation was repeated. By a series of such steps the required total pressure was approached slowly. The pressure in the external bulb could be measured when no pressure change was observed on the manometer on opening the tap to the bulb. The pressure in the main line then equaled that in the bulb. The mixture was left to equilibrate, initially by interdiffusion of the components. This was found to be time-

consuming and not always complete, so efficient mixing of the gases was ensured by the prior addition of small pieces of Teflon to the external bulb which could then be swirled. Different proportions of CO₂ and N₂O were mixed to prepare samples of different concentrations.

3.5.6 SO₂/CO₂ Mixtures

Bulb (B1) was filled with CO₂ gas. Mixtures of different concentrations of SO₂ in CO₂ were prepared in the external bulb (B₂) using an SO₂ gas cylinder following the same procedure as in N₂O/CO₂ mixtures. The CO₂/SO₂ ratio was varied between 5:1 and 1000:1 to identify and discriminate between monomer, dimer and polymer bands.

3.5.7 Ethylene/CO₂ Mixtures

Mixtures of different concentrations of ethylene in CO₂ were prepared following the same procedure as for N₂O/CO₂ mixtures.

3.6 Measuring IR Spectra

Infrared spectra were measured using a Fourier Transform Infrared Spectrometer (Perkin Elmer, model 1720-X) under the conditions of 1 cm⁻¹ resolution and 16 accumulated scans. The spectral region observed was 450-4000 cm⁻¹. The absorptions of the various pollutants chosen for quantitative study were: N₂O around 2248 cm⁻¹, SO₂ around 1333 cm⁻¹, ethylene around 945 cm⁻¹, carbonyl group (C=O) in acetone and

acetaldehyde around 1715 cm^{-1} , and the $\nu(\text{C-O})$ vibration in formic acid and acetic acid around 1260 and 1300 cm^{-1} , respectively.

IR spectra were recorded using the cell described in Section 3.3 and illustrated in Figure 3.2. The cell was connected to the line using rubber tubing and was pumped out. The flask containing the gas mixture was connected to the cell through the deposition point about 3 cm from the substrate surface as shown in Figure 3.4. The section between the two taps was also pumped out. The cell reservoir was filled with liquid nitrogen to cool the window and the gas from the flask was sprayed onto the window very slowly to get an even solid film. This was done by closing tap A and opening tap B slowly. Tap B was then closed and tap A was opened very slowly. This step was repeated a few times to deposit a small amount of the gas each time. The cell was then placed in the FTIR spectrometer chamber and absorbance spectra were obtained for the gas mixture. All the spectra were obtained with baseline and background correction. After each sample, the cell was warmed with a hair dryer while pumping under dynamic vacuum to avoid any condensation of water vapour on the windows.

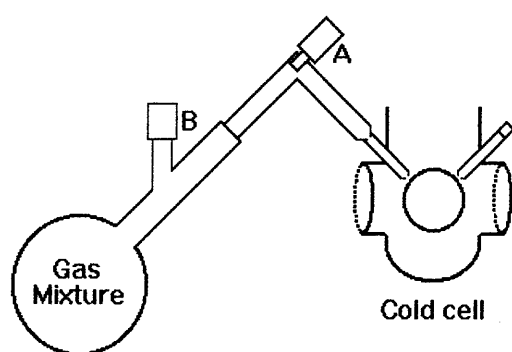


Figure 3.4 Deposition of the gas mixture onto the cold window.

Matrices for calibration purposes were grown from mixtures of known concentration of the species under consideration, X, in CO₂. As the thickness of the matrix was not measured, an infrared absorption band of CO₂ was used as an internal calibrant and all absorbance measurements were made as a ratio of the absorbance of a band of species X to the absorbance of a band of CO₂. The selected absorption of CO₂ used was a band of weak intensity centred at about 2282 cm⁻¹ which arises from the asymmetric stretch of the isotopomer ¹⁶O¹³C¹⁶O present in its natural abundance. The corresponding feature of the abundant isotopomer ¹⁶O¹²C¹⁶O at about 2355 cm⁻¹ is not so useful since its extremely high intensity makes measurement of the intensity difficult or indeed impossible as shown in Figure 3.5. Infrared absorption was measured by integrating the area under an absorption feature. Assuming the Beer's Law to be valid, the ratio of the integrated absorption for feature ν of species X to the absorption of CO₂ at about 2282 cm⁻¹ is calculated. The peak area ratios were plotted against the concentration of the pollutant to get calibration curves.

3.7 Studying isotopic compounds

In Chapter 5 IR spectra of isotopic carbonyl compounds isolated in CO₂ matrix were studied. This was done to study the effect of the CO₂ matrix on the absorptions of the compounds. Four deuterated compounds have been chosen for this study: acetone-*d*₆, acetic acid-*d*, acetic-*d*₃ acid-*d* and formic-*d* acid-*d*. Mixtures of each compound in CO₂ matrices were prepared following the same procedure as for the non deuterated compounds. The IR spectra were recorded, analysed and compared with those of the non deuterated compounds. The differences are discussed in terms of frequency shifts occur with deuteration.

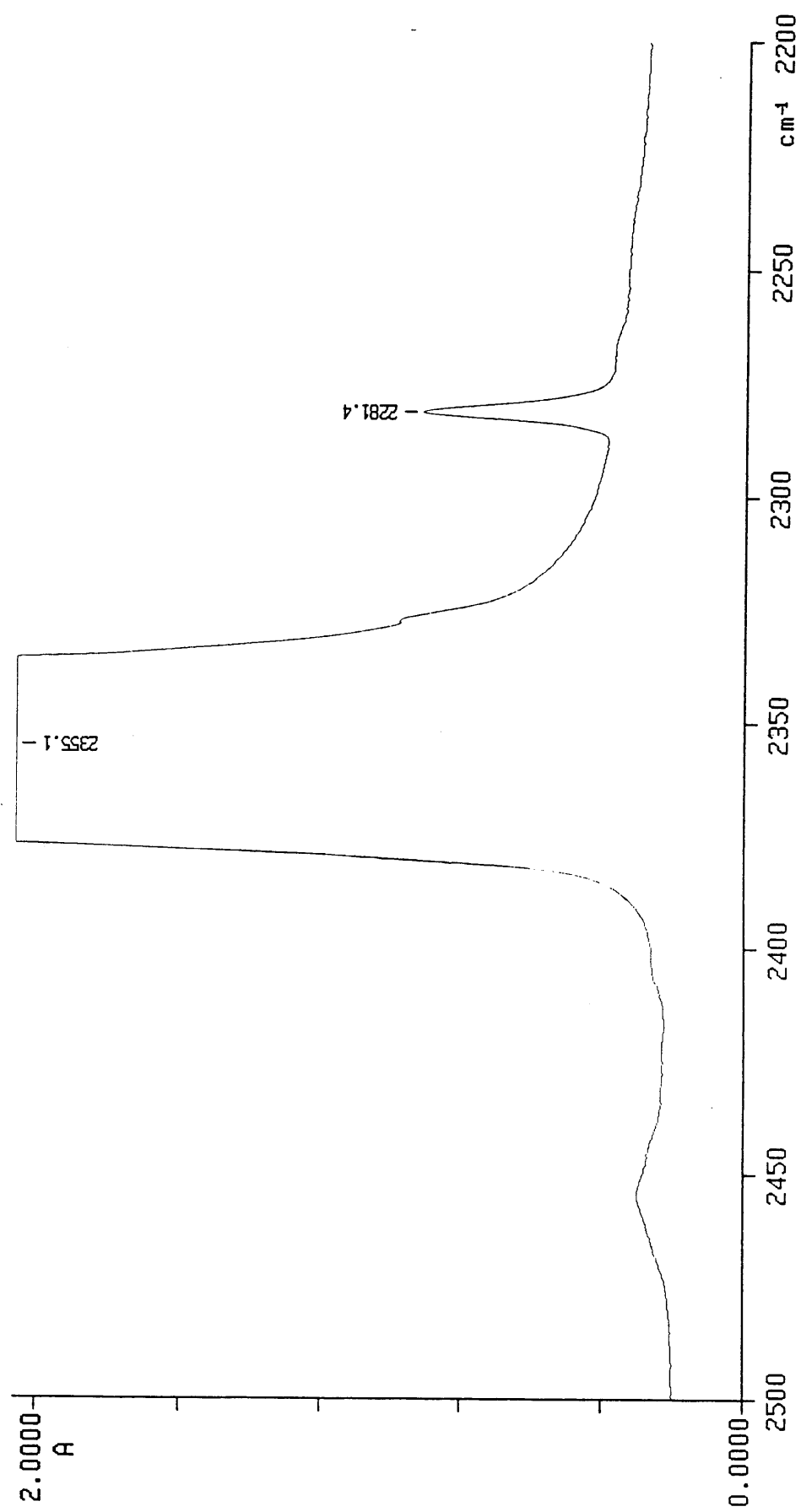


Figure 3.5 IR spectrum showing the ¹³CO₂ absorption (at ~2281 cm⁻¹) used as an internal calibrant.

3.8 Using adsorbents as a pre-concentration technique

In the work reported in Chapter 6 four different types of adsorbent materials (activated carbon, alumina, molecular sieve and kieselguhr) have been studied for adsorbing carbonyl compounds (acetone, acetaldehyde, acetic acid and formic acid). Mixtures of each carbonyl compound in CO₂ have been adsorbed on each of the adsorbents packed into glass tubes, then thermally desorbed and deposited onto the cold window. IR spectra were recorded and compared to those of mixtures of known concentration which had not been separated by the use of an adsorbent. The percentage recoveries were obtained and the adsorbent material that gave the best recovery was chosen to adsorb compounds present in the atmosphere as a pre-concentration technique that can be used in field work.

3.9 Air Sampling using a portable vacuum line

A simple, portable vacuum line illustrated diagrammatically in Figure 3.6 was built for air sampling in the field. A Speedivac high vacuum rotary pump was used for the pumping system. An Edwards Pirani 501 was used with an Edwards Pirani PRE10K gauge head for pressure readings from 10⁻³ to 5 Torr.

Since water is the major collected component in the lower troposphere, it was thought that it must be removed from all the samples because of its own strong, interfering IR spectrum and its broadening effect on other absorption lines, also because of the possibility of forming hydrogen bonds with other reagents. All the sampling and water removing described in this work were done in one step in the field. The bulb in

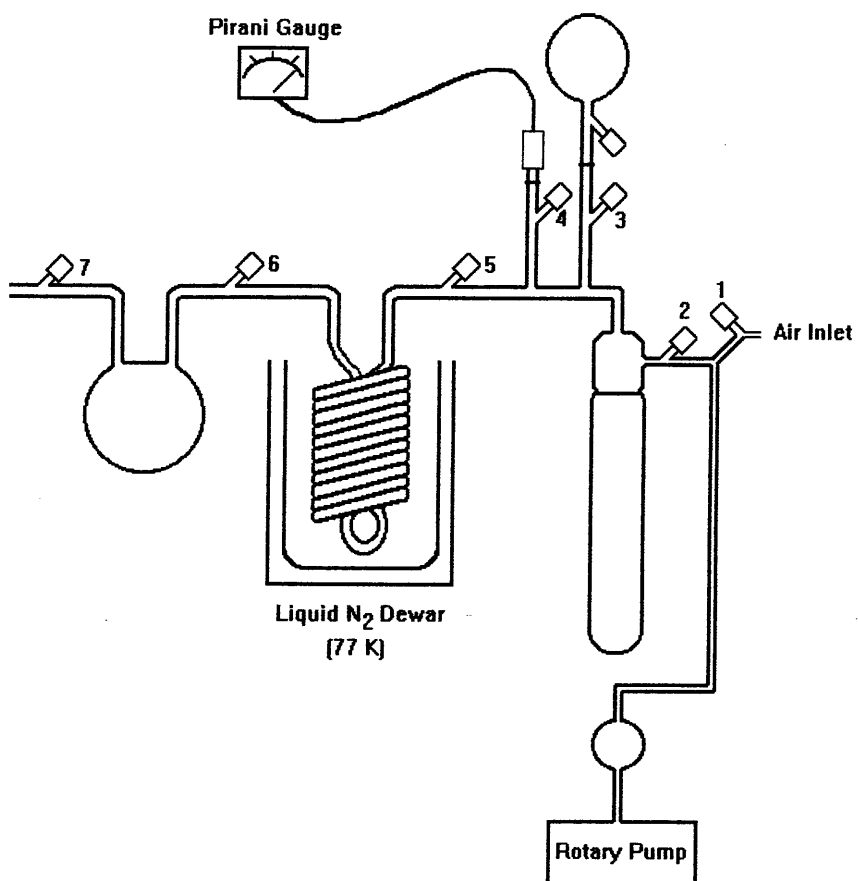


Figure 3.6 The portable vacuum line used for air sampling.

the vacuum line was cooled to -45°C using a chlorobenzene slush bath, while the coil was cooled to 77 K using liquid nitrogen. Air was slowly drawn through the vacuum line so that most of the water is trapped into the bulb while other gases are trapped in the coil. The principal important species which are not collected are N_2 , O_2 , Ar, CH_4 and CO. O_3 and NO may not be quantitatively collected since they both have significant vapour pressures at 77 K. CO_2 has a sufficiently high vapour pressure (2.26×10^5 Torr) at room temperature to permit convenient handling of the gas in a vacuum line and a sufficiently low pressure (1.08×10^{-8} Torr) at 77 K to permit exposure to high vacuum (see Table 3.2).

Table 3.2 Vapour pressures of the studied compounds.

<u>Compound</u>	<u>Vapour Pressure at 77 K</u> <u>(Torr)</u>	<u>Vapour Pressure at 298 K</u> <u>(Torr)</u>
CO_2	1.08×10^{-8}	2.26×10^5
N_2O	2.28×10^{-7}	3.13×10^5
SO_2	a	4.21×10^3
Ethylene	2.00×10^{-3}	8.38×10^4
Acetone	a	2.18×10^2
Acetaldehyde	a	9.83×10^2
Acetic Acid	a	1.52×10
Formic Acid	a	3.08×10
Ozone	3.75×10^{-2}	4.63×10^4
NO	5.20×10^{-2}	2.26×10^7

^a pressures too low to be measured; predicted to be less than 10^{-10} Torr.

The procedure adopted for collecting air samples using the portable vacuum line was as follows:

- The vacuum line was pumped out till the pressure reached 5×10^{-3} Torr on the Pirani gauge.
- A chlorobenzene slush bath Dewar (-45°C) was placed around bulb 1 and a liquid nitrogen Dewar (77 K) was placed around the coil.

- The air inlet tap was opened and all the other taps were controlled so that the flow rate inside the line was very low to allow water vapour to be trapped at -45°C and all other gases to be trapped at 77 K.
- The tap between bulb 1 and the coil was closed and the line was pumped out for 5 minutes while the liquid nitrogen Dewar is around the coil to remove any traces of materials which have a significant vapour pressure at 77 K.
- Tap 2 was closed and the liquid nitrogen Dewar was removed to allow all the frozen gases to warm up to room temperature and to be transferred to an external bulb (2) that has a finger-shape projection which can be surrounded by a liquid nitrogen Dewar to ensure the transfer of all the trapped compounds.
- The external bulb was then connected via flexible vacuum tubing to the cold cell and the gas sample was deposited onto the cold window and an IR spectrum was obtained for that sample.

The sample prepared for matrix growth is thus principally carbon dioxide, the next most abundant constituents normally being N_2O (0.1%) and residual H_2O . It should be noted that some H_2O always passes through the bulb designed to trap it in the procedure described earlier in this section. Water is commonly a constituent of the matrices discussed in this thesis. The mixing ratios of other trace gases are typically in the ppm-to-sub ppm range with respect to CO_2 .

The portable line was tested for fractionating quality. Mixtures of known concentrations of gases in CO_2 were prepared and introduced to the portable line instead of the real air sample by connecting the mixture bulb to the line at tap 7. The above procedure was repeated and the trapped gases were collected in an external bulb and deposited onto the cold window for IR analysis. The IR spectra were compared with those obtained for the same mixtures using the main vacuum line. It was observed that

the ratio of the integrated absorption for feature ν of species X to the absorption of CO₂ at about 2282 cm⁻¹ was lower when the portable line was used for all the mixtures of the studied compounds. Some of the compounds might be pumped out the line which could be due to a relatively high flow rate that not all of the compound was trapped in either temperature. CO₂ could also be thought of being pumped out the line, but this would result in higher compound to CO₂ ratios, and since all the ratios were lowered, the first possibility is more likely to occur. On the other hand, water was not shown to be a great problem if present in small amounts, therefore, it was thought that it does not have to be totally removed from the sample mixtures. The problem of the fractionating quality was believed to be more critical at this stage and other sampling methods were thought to be tried as alternative solutions.

3.10 Collecting air samples in the field

In Chapter 7 work is reported where adsorbent tubes were used to collect air samples in the field. The results obtained from the study of a range of adsorbents (section 3.8) were used to choose the best adsorbent for this purpose. A very simple apparatus was used to draw air samples through the adsorbent tubes (Figure 7.2). The samples were desorbed thermally and IR spectra were recorded as described earlier in Section 3.6. The standard IR spectra obtained as described in Chapter 4 were used for qualitative and quantitative analyses of these spectra.

Reference

1. Shriver, D. F. and Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed. (J. Wiley, Chichester, **1986**).

4.1 Introduction

Attempts to correlate infrared spectra and structure by means of functional group absorption frequencies began many years ago. Today, infrared spectroscopy is one of the most commonly employed spectrometric technique for the characterization of chemical compounds. Despite established interest and activity in this area, infrared spectroscopy does not yet provide a simple and satisfactory approach to the analysis of gas mixtures, especially multicomponent systems. The reason is that infrared gas phase spectra are characteristically rich and often exhibit extensive overlap of spectral lines. Furthermore, gas phase vibration-rotation band contours are sensitive to pressure and temperature.¹

Despite the fact that structurally similar molecules will have similar group frequencies, the frequencies of normal vibrations are extraordinarily sensitive to overall molecular structure. Hence, band overlap in gas phase spectra is caused primarily by the presence of rotational structure. These distributions of spectral intensity result not only in overlap; they serve also to dilute the concentration sensitivity of the spectrometric technique. The method of cryogenic sampling condenses this broad spectral distribution into a single vibrational line.¹

This chapter is divided into two parts. The first part is concerned with a spectroscopic study of the IR spectra of different compounds either in the gas phase, solid phase or isolated in CO₂ matrix. The spectra are discussed in detail in terms of frequency shifts on moving from one phase to another and are compared with the spectra of the CO₂ matrix-isolated spectra to study the behaviour of the compounds in

CO₂ matrix and the efficiency of the CO₂ matrix in isolating the compounds comparing to other conventional matrices used in other studies. In the second part, more IR spectra are studied for mixtures of different concentrations of each compound in CO₂ matrices as a preliminary step to constructing calibration curves for these compounds. Spectral analysis of individual compound is discussed in the following sections.

4.2 Spectral Analysis

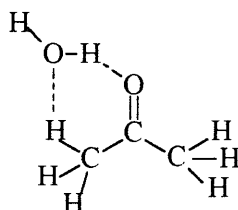
The matrix isolation technique has been applied to infrared spectroscopy with great success, especially in the study of species unstable at room temperature. However, the great amount of work published thereon indicated that there are many difficulties associated with this technique. Frequency shifts, band splittings, polymerization and geometrical distortions are the most common effects observed in matrix work. The best way of rationalizing these effects, apart from theoretical or semiempirical calculations, is by trying to correlate, where possible, gas phase and matrix isolation data in a series of molecules.²

In the current work several compounds have been isolated at 77 K in CO₂ matrices. In most cases spectra have never previously been recorded for these species isolated in CO₂ matrices. It is therefore pertinent to analyse these spectra in some detail and to compare them with spectra obtained for the same compounds in more “conventional” matrices, e.g. argon or nitrogen, and with gas phase or liquid phase spectra. For each compound, full assignments of the bands are given for gas, solid and matrix-isolated spectra. The frequency shifts and the matrix effects are discussed in this section. In general, the frequency shifts are interpreted in terms of different electrostatic interactions between the trapped molecule and the surrounding matrix, and the doublet

in terms of more than one trapping site in the matrix. Other perturbations may arise due to the site symmetry of the trapped species which may cause a splitting of any degenerate vibrations. As discussed in chapter 2 degenerate vibrations (two or more vibrations of the same energy) occur in molecules of high symmetry. Any lowering of this symmetry, e.g. as a result of the site symmetry within the matrix, will lead to a lifting of this degeneracy.

4.2.1 Acetone

The FT-IR absorption spectrum of the hydrogen-bonded acetone-water complex has been investigated in solid argon matrices.³ Acetone and water vapours were co-condensed with an excess of argon gas at 12 K, giving rise to red- or blue-shifted absorptions near most of those associated with the fundamental transitions of matrix-isolated acetone or water. Vibrational shifts are indicative of a 1:1 complex of acetone and water, in which water is hydrogen-bonded to the carbonyl oxygen of acetone. Accordingly, red shifts are observed for the $\nu(\text{C}=\text{O})$ stretching mode of acetone and the $\nu(\text{O}-\text{H})$ stretching modes of water. Computations of the equilibrium structure and fundamental vibration frequencies indicate a cyclic hydrogen-bonded structure involving interactions between water and acetone at both the carbonyl oxygen and one methyl hydrogen as shown in the following structure:



Acetone isolated in an argon matrix has been studied by Dellepiane and Overend.⁴ The acetone was dispersed in an argon matrix at a matrix to active species (M/A) ratio of 600. The samples were contained at liquid helium temperature in a conventional cold cell fitted with CsI windows. The IR spectrum of gas phase acetone shows a strong absorption at about 1360 cm^{-1} but the contour of the band is quite complex and difficult to interpret. The IR spectrum of acetone in an argon matrix shows two very distinct absorptions at 1363 and 1355 cm^{-1} . These absorptions possibly result from lattice splitting of a single fundamental, but since the sample was prepared with an M/A ratio of 400 and no other line appears to be split, Dellepiane *et al.* concluded that these two absorptions correspond to the two fundamentals ν_{16} and ν_5 . There is another band in the matrix spectrum at 1408 cm^{-1} which was assigned to the ν_{15} asymmetric deformation.

The IR spectra of solid and CO_2 matrix isolated acetone recorded in this study are shown in Figures 4.1 and 4.2. All the fundamental frequencies of gaseous, solid and CO_2 matrix-isolated acetone are listed in Table 4.1 along with the frequencies of acetone in argon matrix recorded by Dellepiane *et al.*⁴ for comparison. A comparison between the frequencies of gaseous and solid acetone is shown in Table 4.2 with any frequency shift and splitting, and a similar comparison between gaseous and CO_2 (or Ar) matrix-isolated acetone is shown in Table 4.3.

A very sharp line is observed in the IR spectrum of the CO_2 matrix-isolated acetone at 1710 cm^{-1} and can be assigned to the C=O stretching mode. This line is red shifted by 21 cm^{-1} from the gas-phase compared to a red shift of only 6 cm^{-1} in Ar matrix reported by Dellepiane *et al.* It is possible that this much increased red shift can be explained by a dipole-dipole interaction between the carbonyl group of acetone and the CO_2 . Two doublets are observed at 1440 and 1418 cm^{-1} and at 1366 and 1351 cm^{-1} .

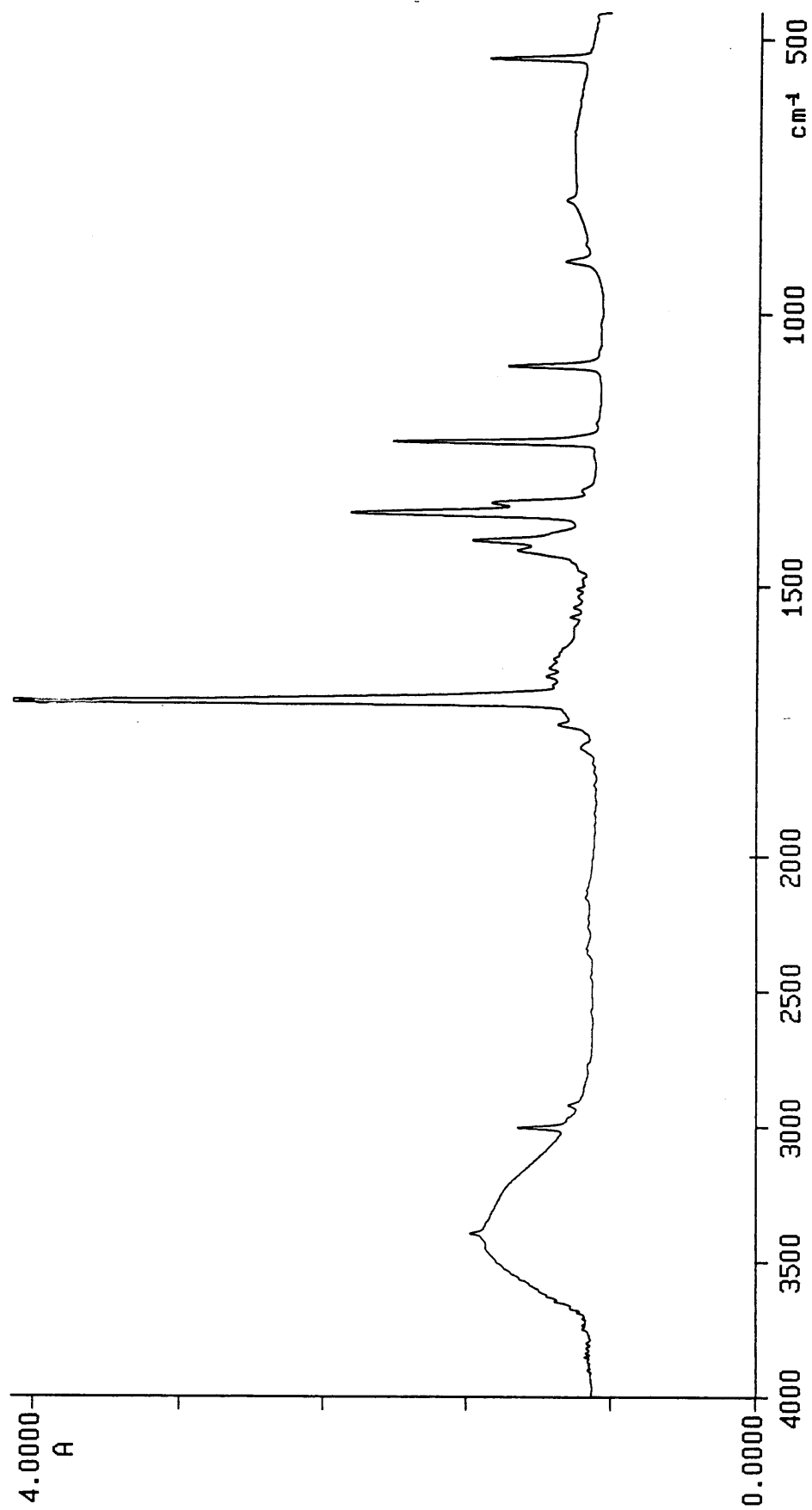


Figure 4.1 IR spectrum of solid acetone.

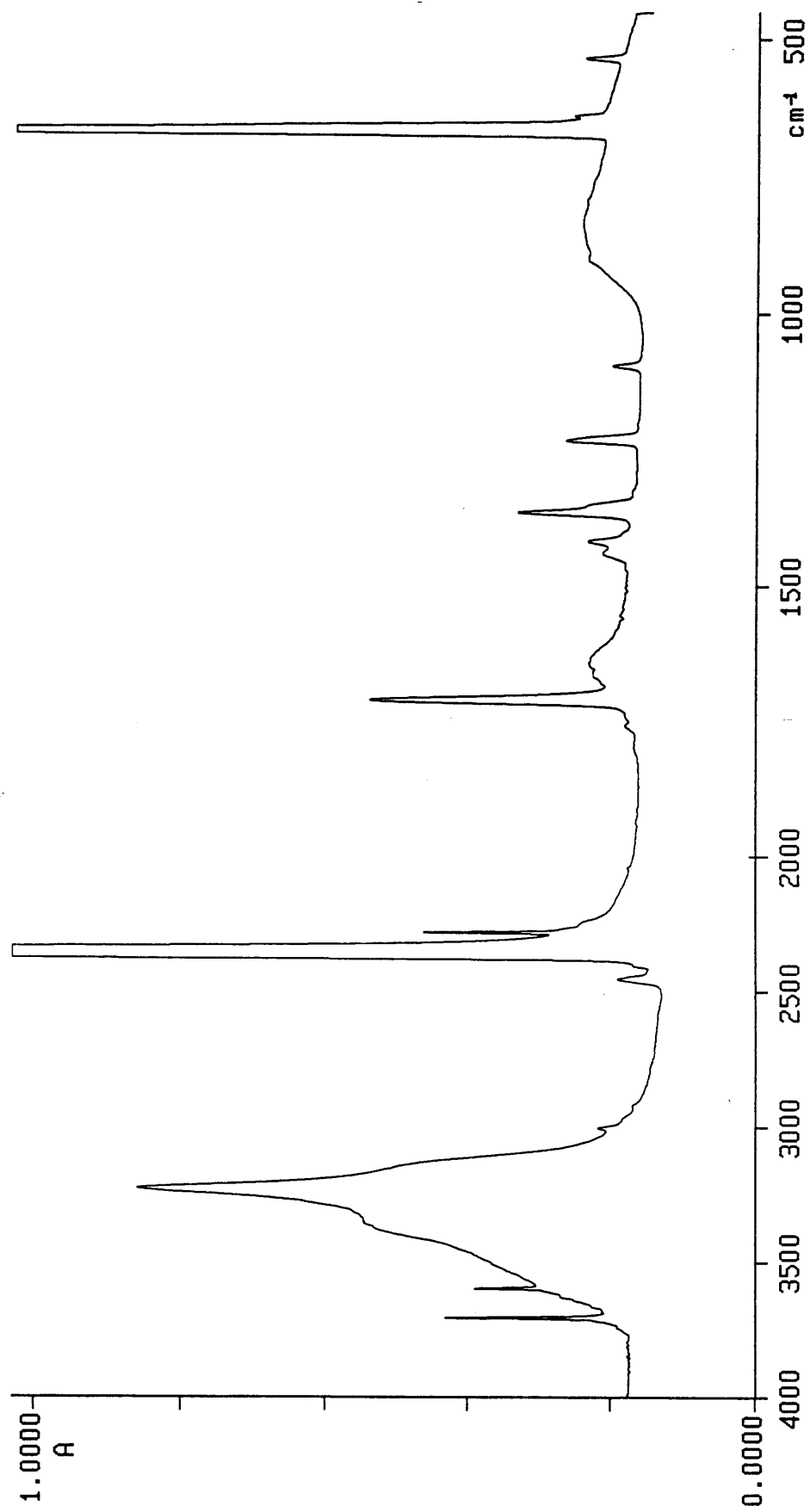


Figure 4.2 IR spectrum of acetone isolated in CO₂ matrix.

These have been assigned to CH bending modes by analogy with Dellepiane's assignment of the corresponding two doublets in the gas phase molecule to the same mode. The centre of the first doublet was red shifted by about 16 cm^{-1} from the centre of the doublet in the gas phase, while the second doublet was red shifted by 29 cm^{-1} . On the other hand, acetone in Ar matrix shows two triplets in this region. The centre of the first triplet does not show any frequency shift from the gas phase while the second triplet shows a red shift of 12 cm^{-1} which is less than that observed in the CO_2 matrix.

Table 4.1 IR frequencies^a of acetone

Mode	Gas ^b	Solid ^c	Matrix-isolated	
			<u>CO_2 matrix^c</u>	<u>Ar matrix^b</u>
$\nu(\text{CH})$	3452	2989	3236	
	3080			
	3019			
	2972			
	2937			
	2867			
$\nu(\text{C=O})$	1731	1717	1710	1725
$\delta(\text{CH})$	1454	1423	1440	1459
	1435	1377	1418	1445
	1410	1351	1366	1430
	1364		1351	1408
				1363
				1355
$\nu_a(\text{CC})$	1216	1263	1235	1217
		1243		
$\delta(\text{CCH})$	1091	1104	1097	1090
	1067	1026		
$\delta(\text{CCH})$	891	918	903	
$\nu_s(\text{CC})$	777	805	843	880
$\delta(\text{CCO})$	530	547	535	530
	484			

^a All frequencies in cm^{-1} .

^b See reference 4.

^c This work (at 77 K).

Table 4.2 Analysis of gaseous and solid acetone spectra^a

<u>Mode</u>	<u>Gas^b</u>	<u>Solid^c</u>	<u>Frequency shift^d</u>	<u>Splitting</u>
$\nu(\text{CH})$	3453 3080 3019 2972 2937 2867	2989	-67	
$\nu(\text{C=O})$	1731	1717	-14	
$\delta(\text{CH})$	1454 1435 1410 1364	1423 1377 1351	-32	46 26
$\nu_a(\text{CC})$	1216	1263 1243	+37	20
$\delta(\text{CCH})$	1091	1104 1026	-26	78
$\delta(\text{CCH})$	891	918	+27	
$\nu_s(\text{CC})$	777	805	+28	
$\delta(\text{CCO})$	530 484	547	+40	

^a All frequencies in cm^{-1} .

^b See reference 4.

^c This work (at 77 K).

^d Average of bands is used for the ν shift calculation.

Table 4.3 Analysis of gaseous and matrix-isolated acetone spectra^a

Mode	Gas ^b	CO ₂ matrix ^c			Ar matrix ^b		
		ν	ν shift ^d	Splitting	ν	ν shift ^d	Splitting
$\nu(\text{CH})$	3453	3236	+181				
	3080						
	3019						
	2972						
	2937						
	2867						
$\nu(\text{C=O})$	1731	1710	-21		1725	-6	
$\delta(\text{CH})$	1454	1440	-16	22	1459	0	14
	1435	1418			1445		15
					1430		
	1410	1366	-29	15	1408	-12	45
	1364	1351			1363		8
					1355		
$\nu_a(\text{CC})$	1216	1235	+19		1217	+1	
$\delta(\text{CCH})$	1091	1097	+6		1090	+1	
$\delta(\text{CCH})$	891	903	+12				
$\nu_s(\text{CC})$	777	843	+66		880	+103	
$\delta(\text{CCO})$	530	535	+28		530	+23	
	484						

^a All frequencies in cm⁻¹.^b See reference 4.^c This work (at 77 K).^d Average of bands is used for the ν shift calculation in case of multiplets.

The asymmetric C-C-C stretching mode in CO₂-matrix-isolated acetone is assigned to the band at 1235 cm⁻¹ showing a blue shift of 19 cm⁻¹ from the gas phase. The symmetric C-C-C stretching mode is observed at 843 cm⁻¹ showing a blue shift of 66 cm⁻¹. The C-C-O bending mode is assigned to the band at 535 cm⁻¹ with a blue shift of 28 cm⁻¹. The argon matrix caused a blue shift of 23 cm⁻¹ to this absorption. In all the absorptions, the CO₂ matrix caused less matrix splitting but larger frequency shifts from the gas phase than did the argon matrix, except for the symmetric C-C-C stretching mode which is blue shifted from the gas phase position by 103 cm⁻¹ in argon matrix by comparison with 66 cm⁻¹ in CO₂ matrix. It seems not unreasonable that a red shift in $\nu(\text{C=O})$ arising from a weakening of the C=O bond (perhaps caused by a dipole-dipole interaction with the CO₂ matrix) should be accompanied by a blue shift in the $\nu(\text{C-C-C})$ modes indicating a strengthening of the C-C bonds.

4.2.2 Acetaldehyde

The IR spectrum of acetaldehyde in a CO₂ matrix is shown in Figure 4.3. The fundamental frequencies of gaseous and CO₂ matrix-isolated acetaldehyde are listed in Table 4.4. The frequencies of gaseous acetaldehyde and their assignments are taken from the results of Thompson and Harris⁵ for the comparison. In general, bands of acetaldehyde show no splitting in the CO₂ matrix. The sharp line observed at 1724 cm⁻¹ is assigned to the C=O stretching vibration with analogy to Thompson *et al.*⁵ who assigned the band at 1720 cm⁻¹ in gas phase acetaldehyde to this mode. The shift of the C=O stretching vibration is only 4 cm⁻¹ but to a higher frequency, inconsistent with the fact that C=O stretching frequency is shifted to a lower frequency as passing from the gas to the liquid to the solid states. It is also not clear why $\nu(\text{C=O})$ of acetaldehyde

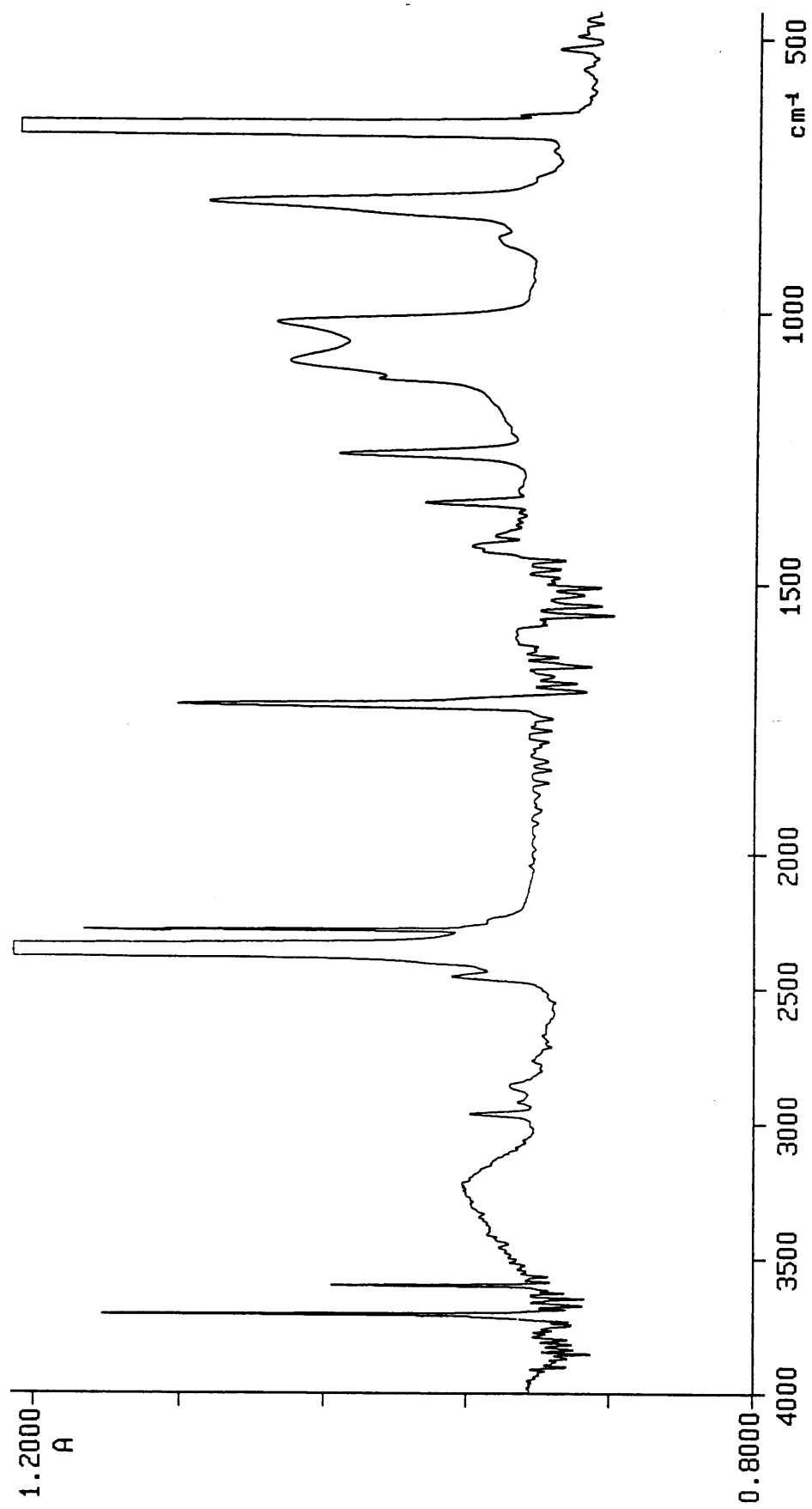


Figure 4.3 IR spectrum of acetaldehyde isolated in CO₂ matrix.

should show a small blue shift in a CO₂ matrix compared to the gas phase whereas the corresponding mode of acetone shows a larger red shift. The CH₃ asymmetric and symmetric stretching modes are observed as sharp peaks at 1351 and 1260 cm⁻¹ in CO₂ matrix, showing red shifts from the positions of the corresponding bands of gas phase acetaldehyde of 54 and 95 cm⁻¹, respectively. The C-C stretching vibration is observed at 1026 cm⁻¹ in CO₂ matrix and it shows the largest frequency shift (+108 cm⁻¹) from the gas phase. The CH₃ rocking mode which was observed by Thompson *et al.* at 883 cm⁻¹ in the gas phase is observed at 799 cm⁻¹ in the CO₂ matrix with a large frequency shift of -84 cm⁻¹.

Table 4.4 Analysis of gaseous and matrix-isolated acetaldehyde spectra^a

<u>Mode</u>	<u>Gas^b</u>	<u>CO₂ matrix^c</u>	<u>Frequency shift</u>
CH ₃ unsym. str.	2976	2948	-28
C=O str.	1720	1724	+4
CH ₃ unsym. bend	1405	1351	-54
CH ₃ sym. bend	1355	1260	-95
C-H wagging	1114	1099	-15
C-C str.	918	1026	+108
CH ₃ rocking	883	799	-84
C-O-O bend	525	534	+9

^a All frequencies in cm⁻¹.

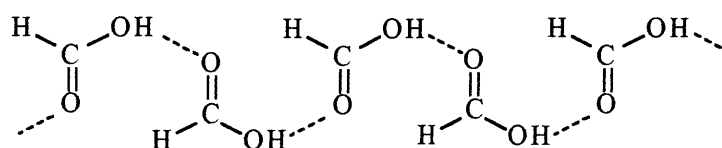
^b See reference 5.

^c This work (at 77 K).

The broad bands observed in the spectrum in the region 1000-1200 cm⁻¹ come from some impurity in or reaction with the CsI windows. They remained upon pumping away the matrix material but disappeared if the external surfaces of the external CsI windows were cleaned with ethanol. They appear in some spectra from time to time but their origin remains uncertain.

4.2.3 Formic Acid

The infrared spectrum of formic acid has received particular attention since it is suggested that this acid, unlike other carboxylic acids, is not dimeric in the liquid or solid state but is associated as a polymer.^{6,7} X-ray analysis⁸ of solid formic acid shows that molecules of formic acid in this state are linked by hydrogen bonds at both ends, forming infinite chains and not dimeric units as shown in the following structure:



Winston and Halford⁹ have pointed out that there is, in general, a correlation between a frequency of the free molecule in the gas and a set of crystalline frequencies, but that both shift of frequency and coupling effects must be taken into account. The spectrum of the solid differs considerably from that of gaseous formic acid, with an increase in the number of absorption bands. Large shifts in frequency occur in hydrogen-bonded structures and are believed to be due to changes in the lengths and force constants of the bonds involved in the hydrogen bonding.

In their study of dimeric and crystalline formic acid, Millikan and Pitzer¹⁰ briefly reported the 3500-2500 cm^{-1} region of a sample trapped in a nitrogen matrix at 20 K. They have noted that the matrix bands are considerably sharper than those of the vapour and that the most intense bands for the dimer lie near the 3100 cm^{-1} peak observed in the vapour. Miyazawa and Pitzer¹¹ have made a detailed comparison of the four isotopic species of formic acid, HCOOH , DCOOH , HCOOD and DCOOD , in the vapour phase and in a nitrogen matrix at 20 K, in the region 800-400 cm^{-1} . They have investigated the internal rotation of formic acid monomer using M/A ratios of 1000 or

3000. They have given assignments for the $\delta(\text{C-H})$ bending, $\delta(\text{OCO})$ bending and the OH(D) torsions for the matrix-isolated monomer. The torsional vibrations of the terminal OH groups of short chain multimers of HCOOH were observed in the matrix at 685 cm^{-1} and 694 cm^{-1} . More information on the IR spectra of the deuterated isotopomers of formic acid is given in Chapter 5.

The IR spectra of gaseous, crystalline and CO_2 matrix-isolated formic acid are shown in Figures 4.4-4.6. The fundamental frequencies of these three phases are listed in Table 4.5 along with the values of the gas and solid phases reported by Millikan⁷ for comparison. In Table 4.6, a comparison between the frequencies of gaseous and solid formic acid is given with the frequency shifts and splittings. In the current work three strong bands were observed for solid formic acid at 2901 , 2734 , and 2579 cm^{-1} which can be assigned to the set of three frequencies associated with the OH stretching vibration; these are in approximate agreement with Chapman's experiments⁶ on solid formic acid which gave IR absorptions at 2902 , 2734 , and 2579 cm^{-1} . The frequencies of the IR absorptions of solid formic acid are given in Table 4.6 where they are compared with the gas phase frequencies. On the assignment of the frequencies of solid formic acid, the shift from the monomer frequency in the vapour (3586 cm^{-1}) to the mean position of the three components in the spectrum of the solid is -848 cm^{-1} . The frequency shift that Chapman obtained was -825 cm^{-1} and he has considered this very large shift to be consistent with the bond lengths observed by X-ray measurements.

The C-H stretching frequency of the solid is expected not to be altered greatly from that observed for the vapour (2939 cm^{-1}) since this bond is not intimately connected with other molecules upon association. It is not possible to observe clearly the C-H stretching frequency of the solid due to overlapping with the broad OH

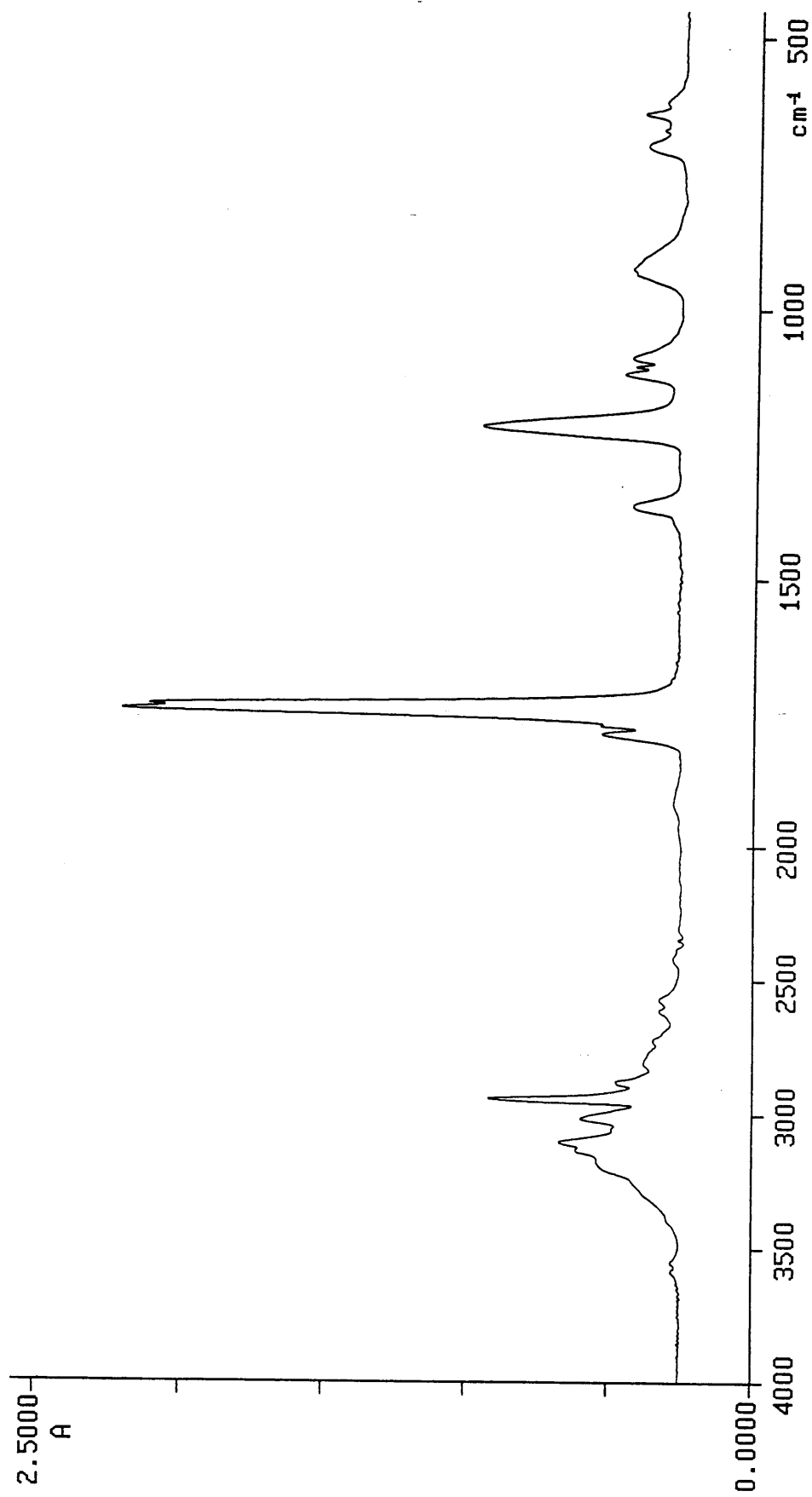


Figure 4.4 IR spectrum of gaseous formic acid.

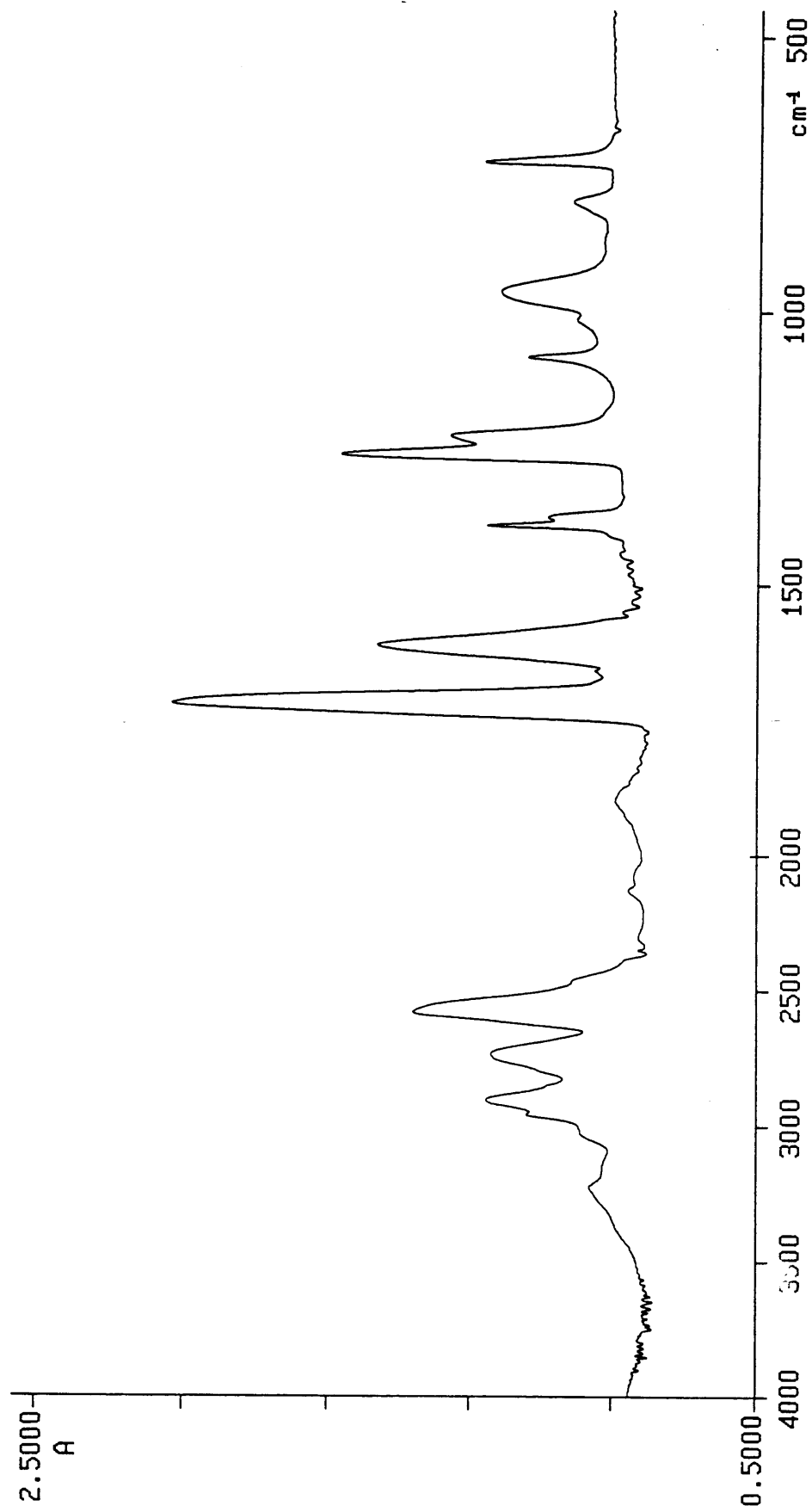


Figure 4.5 IR spectrum of solid formic acid.

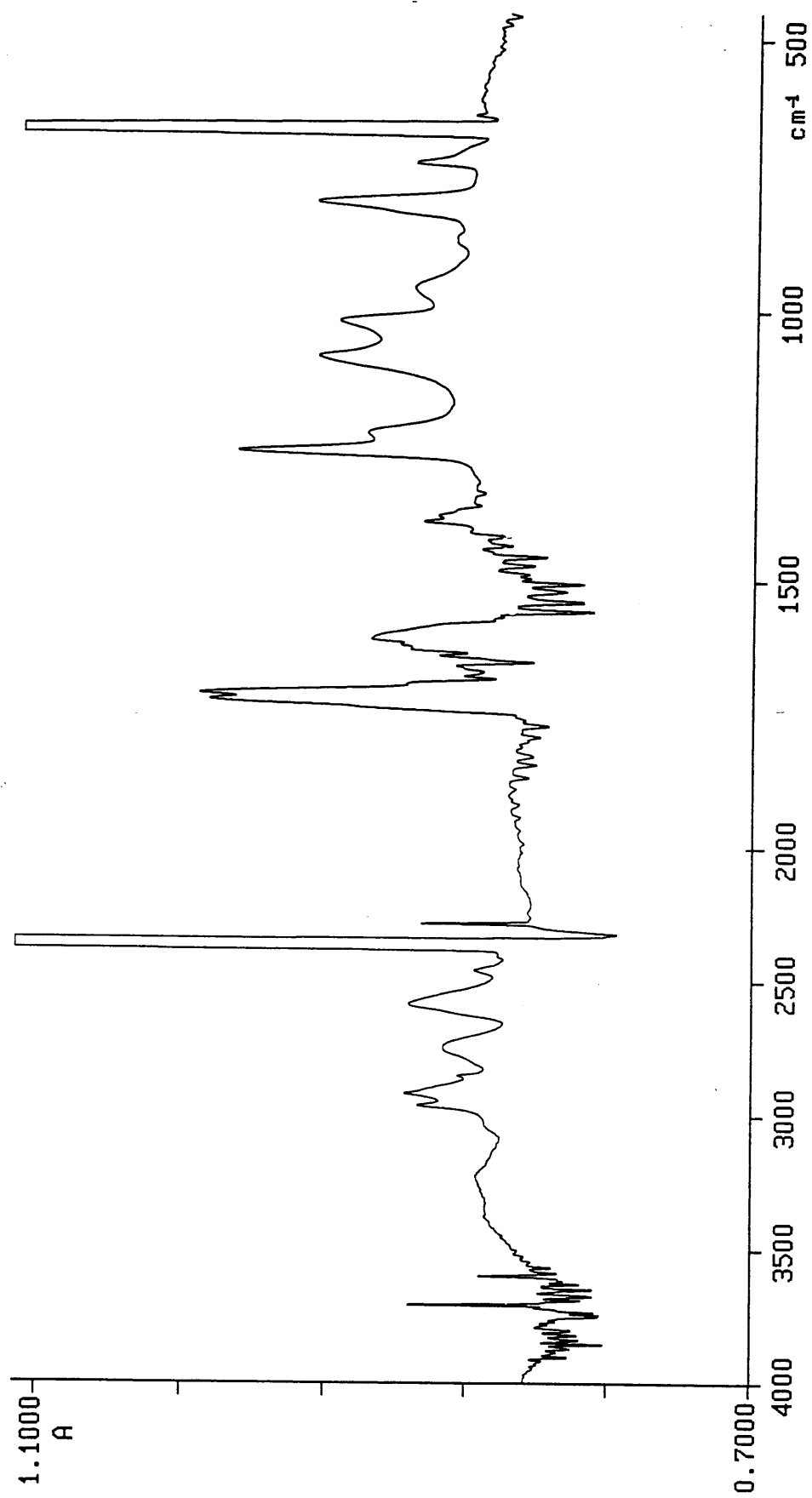


Figure 4.6 IR spectrum of formic acid isolated in CO₂ matrix.

Table 4.5 IR frequencies^a of formic acid

Mode	Gas phase		Solid phase		CO ₂ matrix
	This work	Millikan ^b	This work	Millikan ^b	This work
$\nu(\text{OH})$	3586	3570	2901 2734 2579	2958	2902 2757 2586
$\nu(\text{CH})$	2939	2943	2958	2532	2958
$\nu(\text{C=O})$	1736	1770	1721	1703	1723
$\delta(\text{CH})$	1361	1387	1392 1378	1391 1381 1370	1392 1377
$\delta(\text{OH})$	1218	1229	1262 1227	1255 1224	1261 1225
$\nu(\text{C-O})$	1105	1105	1083	1083	1084
$\delta(\text{CH})$	925	1033	963	974	1014 954
$\delta(\text{O-C=O})$	639	636	727	721	728

^a All frequencies in cm⁻¹.^b See reference 7.**Table 4.6** Analysis of gaseous and solid formic acid spectra^a

Mode	Gas ^b	Solid ^b	Frequency shift ^c	Splitting
$\nu(\text{OH})$	3586	2901 2734 2579	-848	167 155
$\nu(\text{CH})$	2939	2958 (inflexion on side of 2901 cm ⁻¹ band)		
$\nu(\text{C=O})$	1736	1721	-15	
$\delta(\text{CH})$	1361	1392 1378	+24	14
$\delta(\text{OH})$	1218	1262 1227	+27	35
$\nu(\text{C-O})$	1105	1083	-22	
$\delta(\text{CH})$	925	963	+38	
$\delta(\text{OCO})$	639	727	+88	

^a All frequencies in cm⁻¹.^b This work (at 77 K).^c Average of bands is used for ν shift calculation.

absorption in the spectrum. The small peak (at 2958 cm^{-1}) on the side of the 2901 cm^{-1} band may be due to this vibration.

It was reported by Chapman⁶ that electron diffraction and X-ray diffraction measurements indicate that the C=O distance is the same (within a limit of error) in the vapour and the solid states. If this is the case, then the frequency of the carbonyl vibration of the solid would be expected to be near the frequency of the analogous vibration in the gaseous monomer spectrum. The gaseous monomer frequency is observed at 1736 cm^{-1} . The absorption most reasonably assigned to carbonyl vibration of the solid is at 1721 cm^{-1} . This gives a relatively modest shift, $\Delta\nu$, of -15 cm^{-1} on moving from the vapour to the solid indicating presumably a slight reduction in C-O force constant. The frequency assigned to the C-O vibration in the spectrum of the monomer is at 1105 cm^{-1} . The most reasonable assignment of this vibration in the spectrum of the solid is to a band at 1083 cm^{-1} . This again gives a relatively modest shift, $\Delta\nu$, of -22 cm^{-1} on moving from the vapour to the solid.

A comparison between the vapour phase and the CO₂ matrix-isolated frequencies is given in Table 4.7 with the frequency shifts and splittings. The spectra of formic acid in CO₂ matrices principally show similarities to that of solid formic acid. These similarities are noted in both the $\nu(\text{O-H})$ and $\nu(\text{C=O})$ regions (Table 4.5). The concentration of formic acid in different mixtures with CO₂ has little effect on the absorptions. The mixtures with 7% or more formic acid in CO₂ show a maximum frequency shift of 15 cm^{-1} from the band of the solid. The mixtures of 3.5% or less formic acid in CO₂ mostly show only weak characteristic absorptions of formic acid such as the 1255 cm^{-1} band ($\nu(\text{C-O})$) which was used for the data analysis and calculation of peak area ratio. The splittings of $\delta_{\text{sym}}(\text{OH})$ and $\delta_{\text{asym}}(\text{CH})$ were less pronounced at lower concentrations of formic acid since the matrix site effect is less

pronounced with a smaller number of analyte molecules. The spectra of all the mixtures *suggest* that formic acid is present as a polymer in all the concentrations studied. The fact that the association of the formic acid does not appear to vary significantly with change of concentration makes interpretation of the spectra for atmospheric analysis more straightforward.

Table 4.7 Analysis of gaseous and matrix-isolated formic acid spectra^a

<u>Mode</u>	<u>Gas^b</u>	<u>CO₂ matrix^b</u>	<u>Frequency shift^c</u>	<u>Splitting</u>
ν(OH)	3586	2902	-838	145 171
		2757		
		2586		
ν(CH)	2939	2958	+19	
ν(C=O)	1736	1712	-24	
δ(CH)	1361	1392	+24	15
		1377		
δ(OH)	1218	1261	+25	36
		1225		
ν(C-O)	1105	1084	-21	
δ(CH)	925	1014	+59	60
		954		
δ(OCO)	639	728	+89	

^a All frequencies in cm⁻¹.

^b This work (at 77 K).

^c Average of bands is used for ν shift calculation.

There are two suggestions for the large shift in the frequency of the OH band in the spectra of the CO₂ matrix isolated formic acid. The first suggestion is the formation of a hydrogen bond between the OH group in one molecule of formic acid and the carbonyl oxygen in another molecule forming a dimeric species. The second suggestion is the formation of a hydrogen bond between the OH group in formic acid and the oxygen atom in the CO₂ matrix. The spectrum of isolated formic acid generally shows a

dimeric or polymeric character. If the first suggestion is true, then dimeric or polymeric formic acid would be formed only at high concentrations of formic acid in CO₂ and the spectrum of formic acid would not show any dimeric or polymeric character at low concentrations. However, the spectrum of isolated formic acid, at all concentrations, shows dimeric or polymeric character (in the $\nu(\text{OH})$ and $\nu(\text{C=O})$ regions), even at a very low concentrations (0.5%). This leads one to consider the other suggestion that the hydrogen bond is formed between the OH group in formic acid and the oxygen atom in the CO₂ matrix. This suggestion would explain the independence of the OH shift on the concentration of formic acid in CO₂. If the second hypothesis is true then it would be a disadvantage that could limit the use of CO₂ as a matrix material as it is not totally inert. To test this hypothesis it was decided to use other compounds as the matrix material for formic acid at the same concentrations and same temperature (77 K). Toluene was chosen as a suitable material as it will not form any hydrogen bonds with formic acid and it is a rigid solid at 77 K. Initially it was decided to use low concentrations of formic acid in toluene so as to allow little chance for the formation of dimeric species.

Mixtures of different concentrations of formic acid in toluene were prepared and deposited onto the cold window at 77 K. The spectrum of solid toluene is shown in Figure 4.7 for comparison. The spectra of 5% and 50% formic acid in toluene in the solid phase are shown in Figures 4.8 and 4.9, respectively. At low concentration only the toluene absorptions are observed while at high concentration the formic acid absorptions are well-resolved and they show some frequency shifts from the gas phase as shown in Table 4.8. The OH absorption occurs as a triplet at 2913, 2734 and 2578

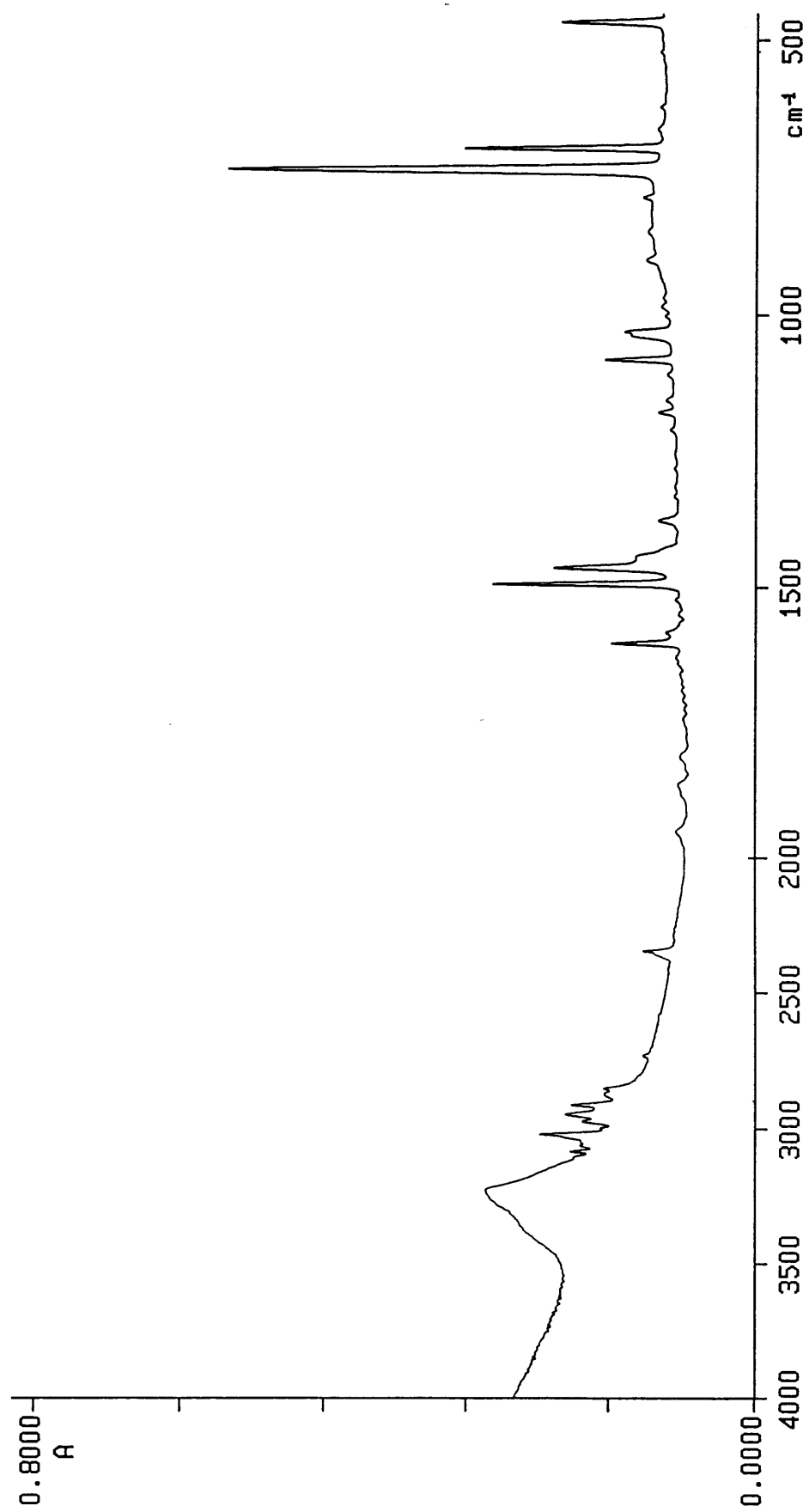


Figure 4.7 IR spectrum of solid toluene.

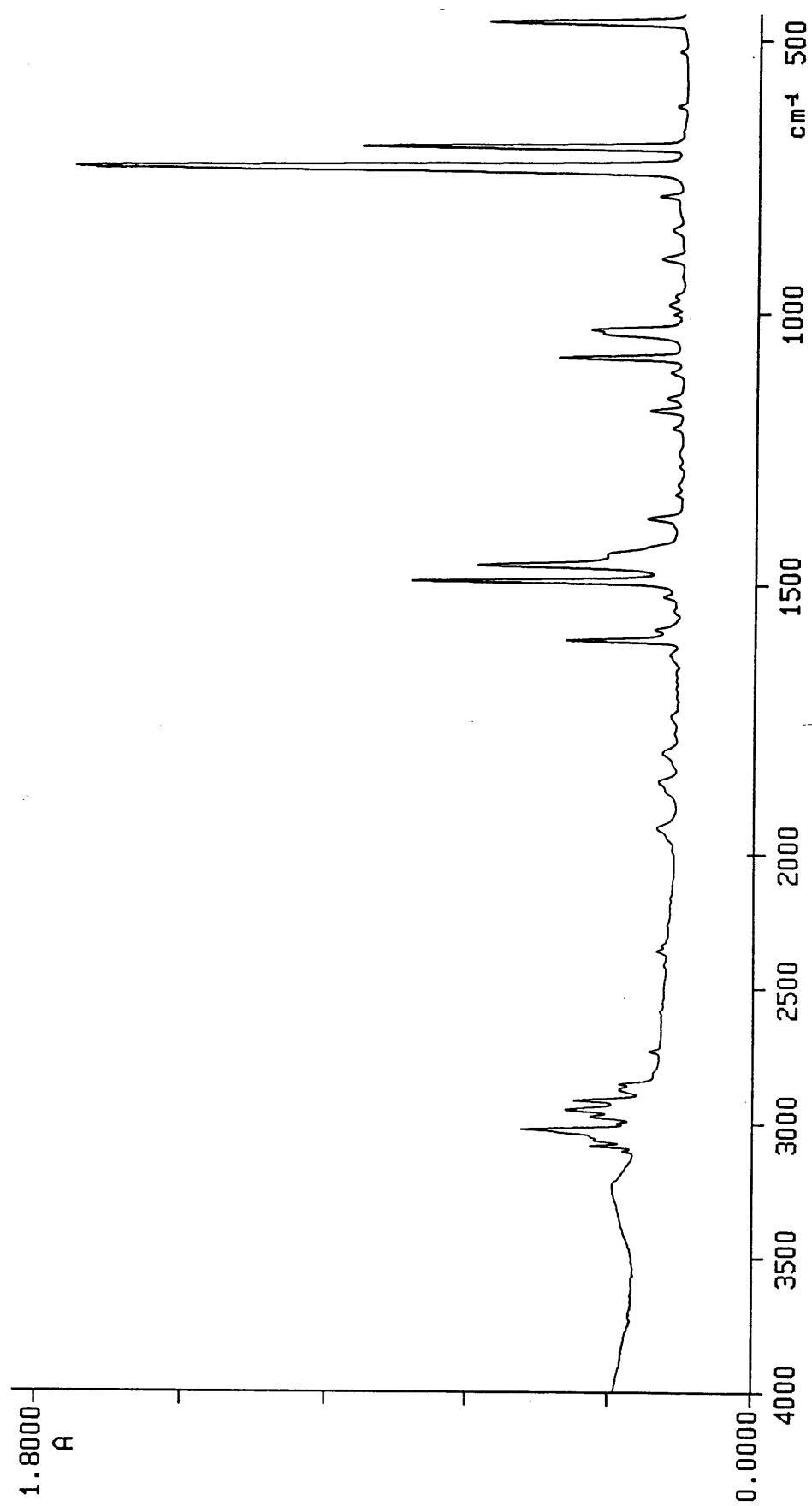


Figure 4.8 IR spectrum of 5% formic acid in solid toluene (at 77 K).

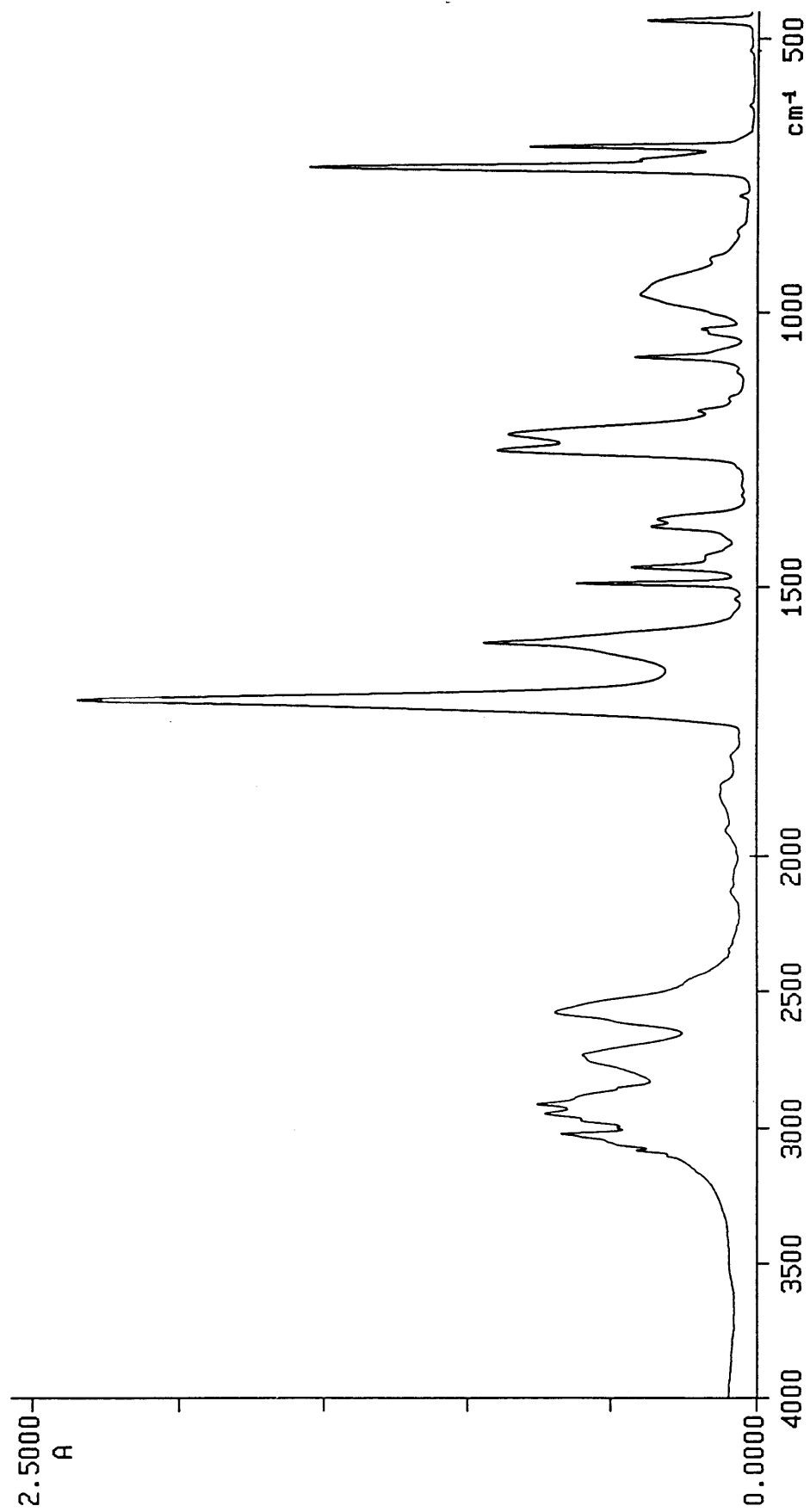


Figure 4.9 IR spectrum of 50% formic acid in solid toluene (at 77 K).

cm⁻¹. The mean position of these lines shows a red shift of 844 cm⁻¹ from the gas phase value. As there is no possibility of the formation of hydrogen bond between formic acid and toluene, the large shift in the OH frequency can only be explained by a hydrogen bonding between two molecules of formic acid to form a dimeric species. At low concentration this is not observed. Unfortunately, however, it was not possible to observe bands of formic acid at low concentrations in toluene matrices so it has not been possible to confirm unequivocally whether shifts in the OH stretching frequency of formic acid arise from hydrogen bonding between formic acid and CO₂ molecules or from hydrogen bonding between neighbouring formic acid molecules. The fact that hydrogen-bonding is seen at all in a toluene matrix does suggest, however, that the second hypothesis is more likely to be true.

Table 4.8 Analysis of the spectrum of formic acid in toluene^a

Mode	Gas ^b	CO ₂ matrix ^b	Toluene ^c	Frequency shift ^d
ν(OH)	3586	2902	2913	-844
		2757	2734	
		2586	2578	
ν(CH)	2939	2958	2948	+9
ν(C=O)	1736	1712	1710	-26
δ(CH)	1361	1392	1391	+24
		1377	1378	
δ(OH)	1218	1014	967	-251
		954		
ν(C-O)	1105	1261	1252	+133
		1225	1223	
δ(CH)	925	1084	1082	+157
δ(OCO)	639	728		

^a All frequencies in cm⁻¹.

^b This work (at 77 K).

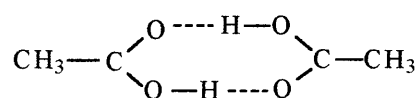
^c Vibrational frequencies of formic acid in toluene at 77 K.

^d ν shifts of formic acid in toluene from the gas phase. Average of bands is used for calculation.

4.2.4 Acetic Acid

An assignment of the fundamental frequencies of acetic acid between 4000 and 400 cm^{-1} is proposed by Berney *et al.*¹² in their IR studies of the four species $\text{CH}_3\text{COOH(D)}$ and $\text{CD}_3\text{COOH(D)}$ isolated as monomers in argon and nitrogen matrices at 4 K. The interference caused by overlapping absorptions in vapour-phase studies was eliminated and the matrix spectra yield clear monomer absorptions in all spectral regions. The study of Redington and Lin,¹³ on the other hand, shows a detailed examination of the hydroxyl stretching region of CH_3COOH matrix-isolated in neon and argon at 5 K and fundamental frequencies for the cyclic dimer ring vibrations are suggested. The results of Grenie *et al.*,¹⁴ who have reported the spectra of CH_3COOH dimers in an argon matrix at 20 K, do not agree with Redington and Lin's assignment. They have pointed out, however, that it is difficult to correlate clearly the gas and matrix frequencies in the 3200-2700 cm^{-1} region as the whole set of absorptions is lowered in intensity and frequency relative to the bands observed between 2500 and 2700 cm^{-1} when going from gas to matrix phase. The IR spectra of monomeric and dimeric acetic acid in the gas phase have been studied by Weltner.¹⁵

Solid acetic acid is suggested to be in the dimeric form as the molecules are hydrogen-bonded as in the following structure:



The IR spectra of solid and CO_2 matrix-isolated acetic acid are shown in Figures 4.10 and 4.11, respectively. The fundamental frequencies of the gaseous, solid and CO_2

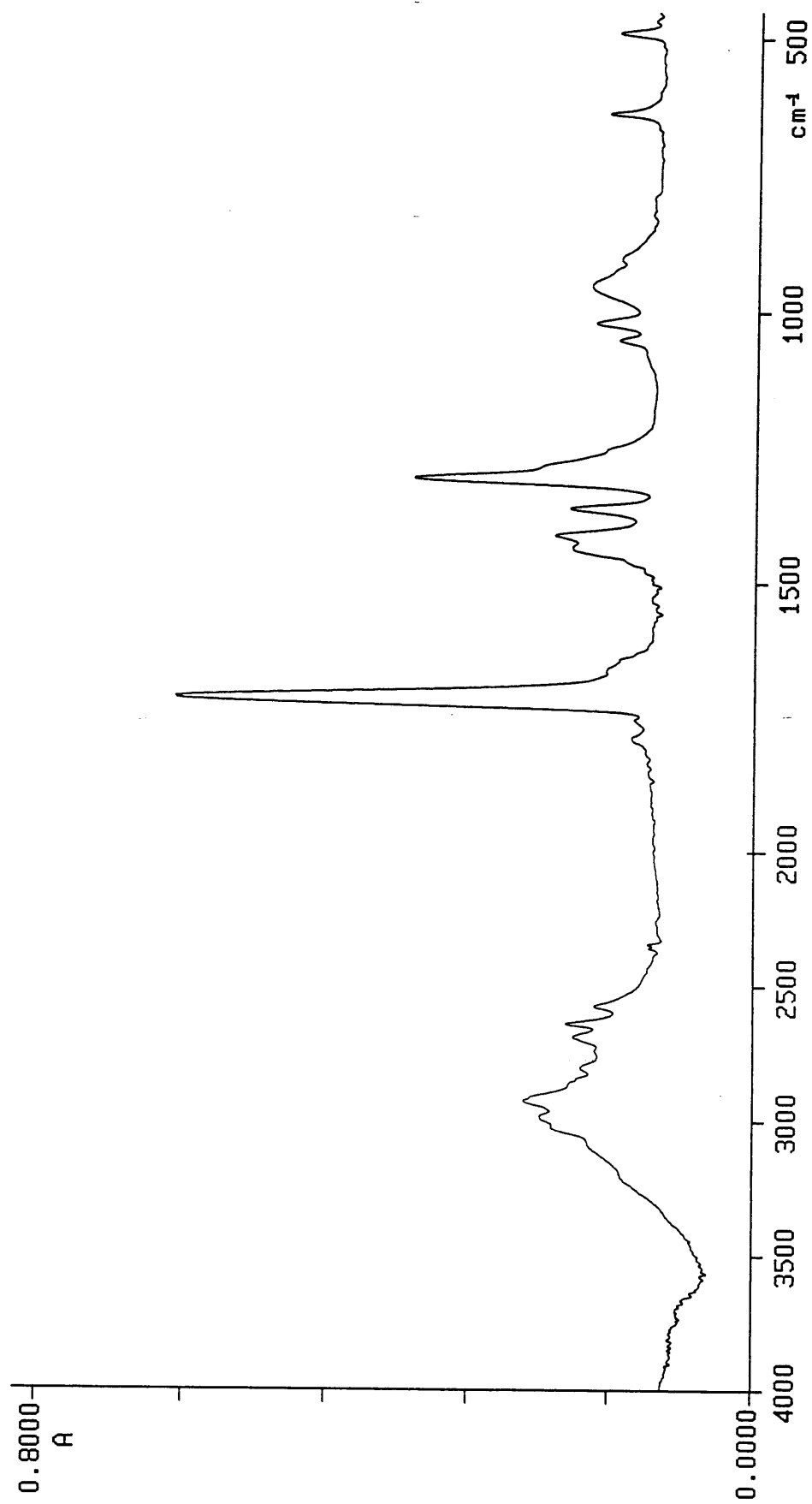


Figure 4.10 IR spectrum of solid acetic acid.

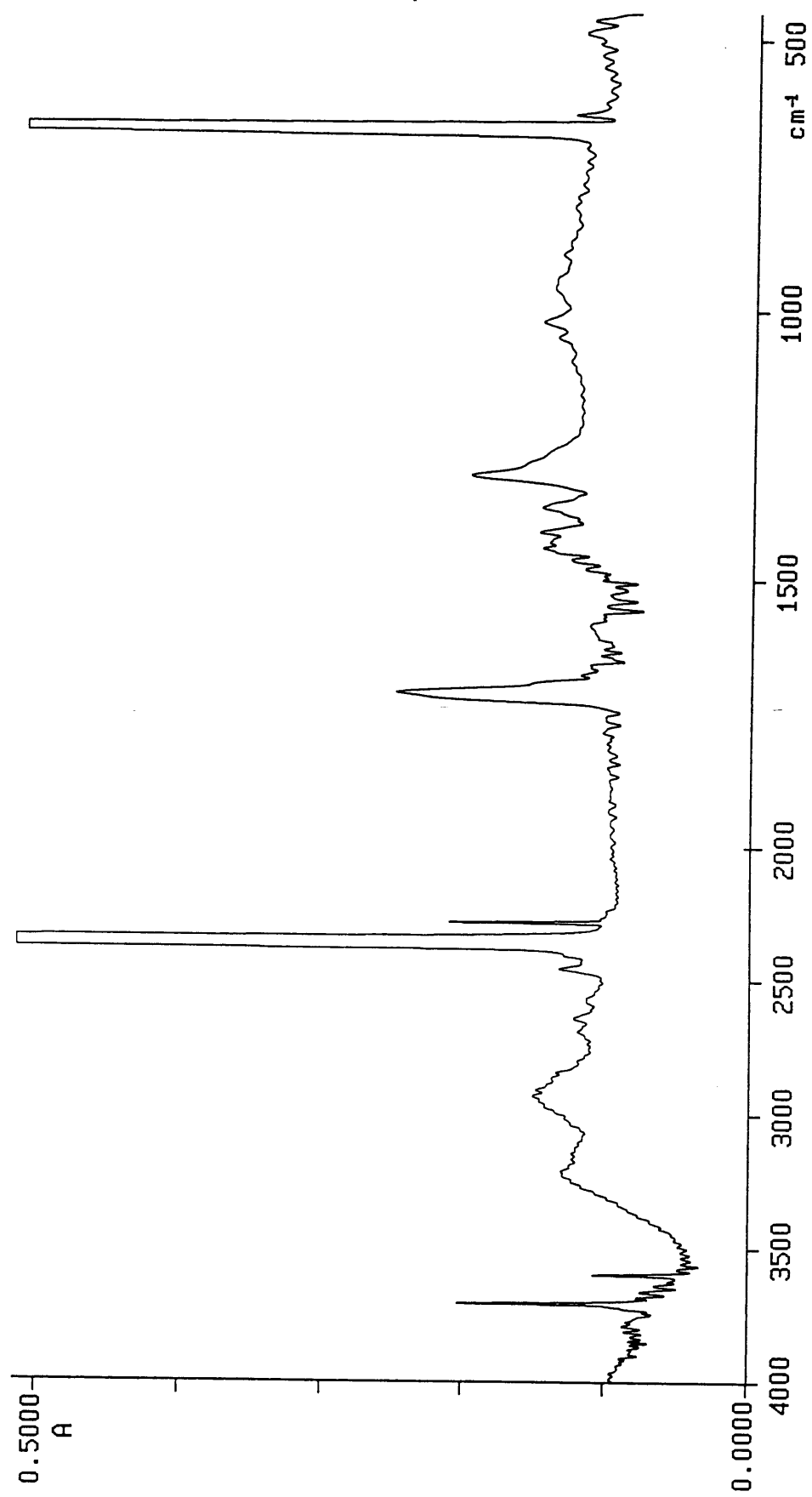


Figure 4.11 IR spectrum of acetic acid isolated in CO₂ matrix.

matrix-isolated acetic acid are listed in Table 4.9. The values of Weltner¹⁵ of monomeric and dimeric acetic acid and their assignments are used for comparison with the CO₂ matrix-isolated acetic acid studied in this work. Table 4.10 shows the comparison between the monomeric, dimeric and the solid acetic acid along with the frequency shifts and the splittings. A similar comparison between the monomeric, dimeric and the CO₂ matrix-isolated acetic acid is given in Table 4.11.

The sharp line observed at 1716 cm⁻¹ in the IR spectrum of the solid acetic acid can be assigned to the C=O stretching vibration. This frequency is closer to that of the dimeric C=O stretching vibration as the frequency shift from the gas phase is -23 cm⁻¹ compared to the shift from the monomeric vibration which is -54 cm⁻¹. The C-O stretching mode is assigned to the line at 1308 cm⁻¹, and its frequency is also closer to that of the dimeric species with a frequency shift from the gas phase of +14 cm⁻¹ compared to +24 cm⁻¹ for the monomeric frequency. The C-C stretching mode in the solid phase is assigned to the broad peak at 950 cm⁻¹. This frequency lies between the frequencies of the monomeric species (996 cm⁻¹) and that of the dimeric species (928 cm⁻¹) but it is closer to that of the dimeric species.

The spectra of acetic acid in CO₂ matrices show some similarities to that of monomeric species and some similarities to that of dimeric species. The absorption of the C=O stretching vibration is observed at 1712 cm⁻¹ with a red shift of 27 cm⁻¹ from the dimer frequency compared to a red shift of 58 cm⁻¹ from the monomer frequency. The sharp peak at 1307 cm⁻¹ is assigned to the C-O stretching vibration. This frequency is closer to that of the dimeric species as the frequency shift is +13 compared to the shift from the monomeric vibration which is +23 cm⁻¹. The O-H stretching vibration, on the other hand, is observed at 3599 cm⁻¹ with a blue shift of only 53 cm⁻¹ from the monomer frequency compared to a blue shift of 609 cm⁻¹ from the dimer frequency. The C-C

Table 4.9 IR frequencies^a of acetic acid

Mode	<u>Gas</u>		<u>Solid^c</u>	<u>CO₂ matrix^c</u>
	<u>Monomer^b</u>	<u>Dimer^b</u>		
O-H str.	3546	2990	-	3599
CH ₃ unsym. str.	3027	3030	2993	3216
CH ₃ sym. str.	2935	-	2925	2933
C=O str.	1770	1739	1716	1712
CH ₃ unsym. bend	1431	-	1438 1413	1441 1413
CH ₃ sym. bend	1381	1371	1364	1366
C-O str.	1284	1294	1308	1307
CH ₃ rock	1184	1066	1052 1021	1019
C-C str.	996	928	950	954

^a Frequencies in cm⁻¹.^b See reference 15.^c This work (at 77 K).**Table 4.10** Analysis of gaseous and solid acetic acid spectra^a

<u>Mode</u>	<u>Monomer^b</u>	<u>Solid^c</u>	<u>ν shift^d</u>	<u>Dimer^b</u>	<u>Solid^c</u>	<u>ν shift^d</u>	<u>Splitting</u>
O-H str.	3546			2990	-		
CH ₃ asym. str.	3027	2993	-34	3030	2993	-37	
CH ₃ sym. str.	2935	2925	-10	-	2925		
C=O str.	1770	1716	-54	1739	1716	+23	
CH ₃ asym. bend	1431	1438 1413	-6	-	1438 1413		25
CH ₃ sym. bend	1381	1364	-17	1371	1364	-7	
C-O str.	1284	1308	+24	1294	1308	+14	
CH ₃ rock	1184	1052 1021	-147	1066	1052 1021	-29	31
C-C str.	996	950	-46	928	950	+22	

^a all frequencies in cm⁻¹.^b See reference 15.^c This work (at 77 K).^d Average of bands is used for ν shift calculation.

stretching vibration is assigned to the frequency at 954 cm^{-1} . This lies between the frequency of the monomeric and that of the dimeric species showing a red shift of 42 cm^{-1} from the earlier and a blue shift of 26 cm^{-1} from the latter species.

Table 4.11 Analysis of gaseous and matrix-isolated acetic acid spectra^a

Mode	Monomer ^b	MI ^c	ν shift ^d	Dimer ^b	MI ^c	ν shift	Splitting
O-H str.	3546	3599	+53	2990	3599	+609	
CH ₃ unsym. str.	3027	3216	+189	3030	3216	+186	
CH ₃ sym. str.	2935	2933	-2	-	2933		
C=O str.	1770	1712	-58	1739	1712	-27	71
CH ₃ unsym. bend	1431	1441 1413	-4	-	1441 1413		28
CH ₃ sym. bend	1381	1366	-15	1371	1366	-5	
C-O str.	1284	1307	+23	1294	1307	+13	
CH ₃ rock	1184	1019	-165	1066	1019	-47	
C-C str.	996	954	-42	928	954	+26	

^a all frequencies in cm^{-1} .

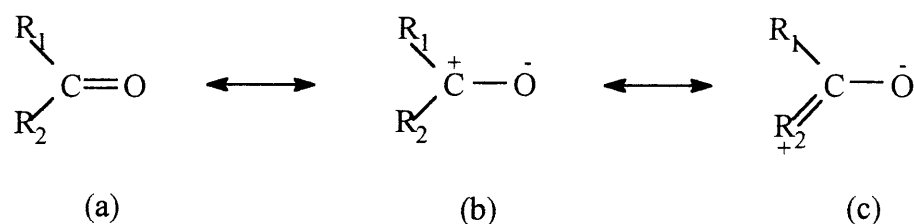
^b See reference 15.

^c This work (at 77 K).

^d Average of bands is used for ν shift calculation.

4.2.5 General matrix effects for organic carbonyl and hydroxy compounds

There is a general lowering of the frequency of the carbonyl group in passing from the vapour to the liquid and the solid states. With most compounds the lowering is about 20 cm^{-1} , but with acids, amides and monosubstituted amides, where hydrogen bridge formation is more directly possible, it is much more pronounced.¹⁶ This fact is true for aldehydes and ketones which may be represented by three different resonance structures:



In ketones (a), the double-bond character may be reduced by participation in the actual molecule of the ionic forms (b) and (c). In alkyl ketones, having a vapour frequency close to 1740 cm^{-1} , the structure (b) must be at least partially contributing to the overall structure. In the aldehydes the presence of the polarisable hydrogen atom leads to diminution of the ionic character, i.e., a smaller proportion of (b), so that the frequency rises (1752 cm^{-1} for acetaldehyde vs. 1742 cm^{-1} for acetone).

IR studies of the complexes between trifluoroacetic acid and acetone in the gas phase and in argon matrices have been made by Wierzejewska *et al.*¹⁷ The effect of the matrix on the complex was studied on the $\nu(\text{OH})$ vibration. In the gas phase, the maximum of this band appears at 3060 cm^{-1} with three sub-maxima at 2720 , 2580 and 2450 cm^{-1} . In the matrix spectrum the band of the strongest intensity is shifted to 2920 cm^{-1} whereas the two submaxima are only slightly affected by matrix environment and occur at 2735 and 2586 cm^{-1} . The submaximum which appears at 2450 cm^{-1} in the gas phase spectra is not observed in the corresponding matrix spectra. The relatively large shift of the $\nu(\text{OH})$ band towards lower frequencies when going from the gas phase to argon matrix reflects the sensitivity of the hydrogen bond to the molecular environment. The internal vibrations of monomeric molecules are only slightly perturbed when the molecule is isolated in an argon matrix.

4.2.6 N₂O

Compounds other than carbonyl compounds such as N₂O and SO₂ (see Section 4.2.7) are studied in this work in order to understand their behaviour in CO₂ matrix as their spectra have never been recorded in this medium. If CO₂ matrices are to be used for the quantitative analysis of these compounds it is first necessary to understand qualitatively the effect of the CO₂ matrix upon the spectra. As part of an experiment done by Spiker *et al.*¹⁸ in which Li atoms were reacted with N₂O in an N₂ matrix, a blank experiment was run in which a sample of N₂O gas was deposited with excess nitrogen and with no lithium atoms. The resulting absorptions were compared with those for solid and gaseous N₂O as reported by Dows¹⁹ and Begun and Fletcher²⁰, respectively. It was found that, except for two broad, weak absorptions around 2265 and 2329 cm⁻¹, the other absorptions at 589, 1167, 1291, 2236 and 2576 cm⁻¹ corresponded rather closely to those already reported for N₂O.

A detailed examination of N₂O isolated in a nitrogen matrix at 15 K has been reported by Smith *et al.*²¹ The observed fundamental frequencies have been compared with the gas phase frequencies and small shifts were observed. The IR spectra of solid and CO₂ matrix isolated N₂O are shown in Figures 4.12 and 4.13, respectively. The fundamental frequencies of the solid and the CO₂ matrix isolated N₂O are listed in Table 4.12. The values of Smith for gaseous and N₂ matrix-isolated N₂O are used for comparison. In the IR spectrum of the solid N₂O, three bands are observed. The assignments of these bands are shown in Table 4.13. The first one is a sharp line at 2246 cm⁻¹ which has the highest intensity and is assigned to the ν_3 absorption with analogy to Smith's assignment for the gas phase frequencies. This absorption is blue shifted from its position in the gas phase by 22 cm⁻¹. The second band shows two lines. A sharp one

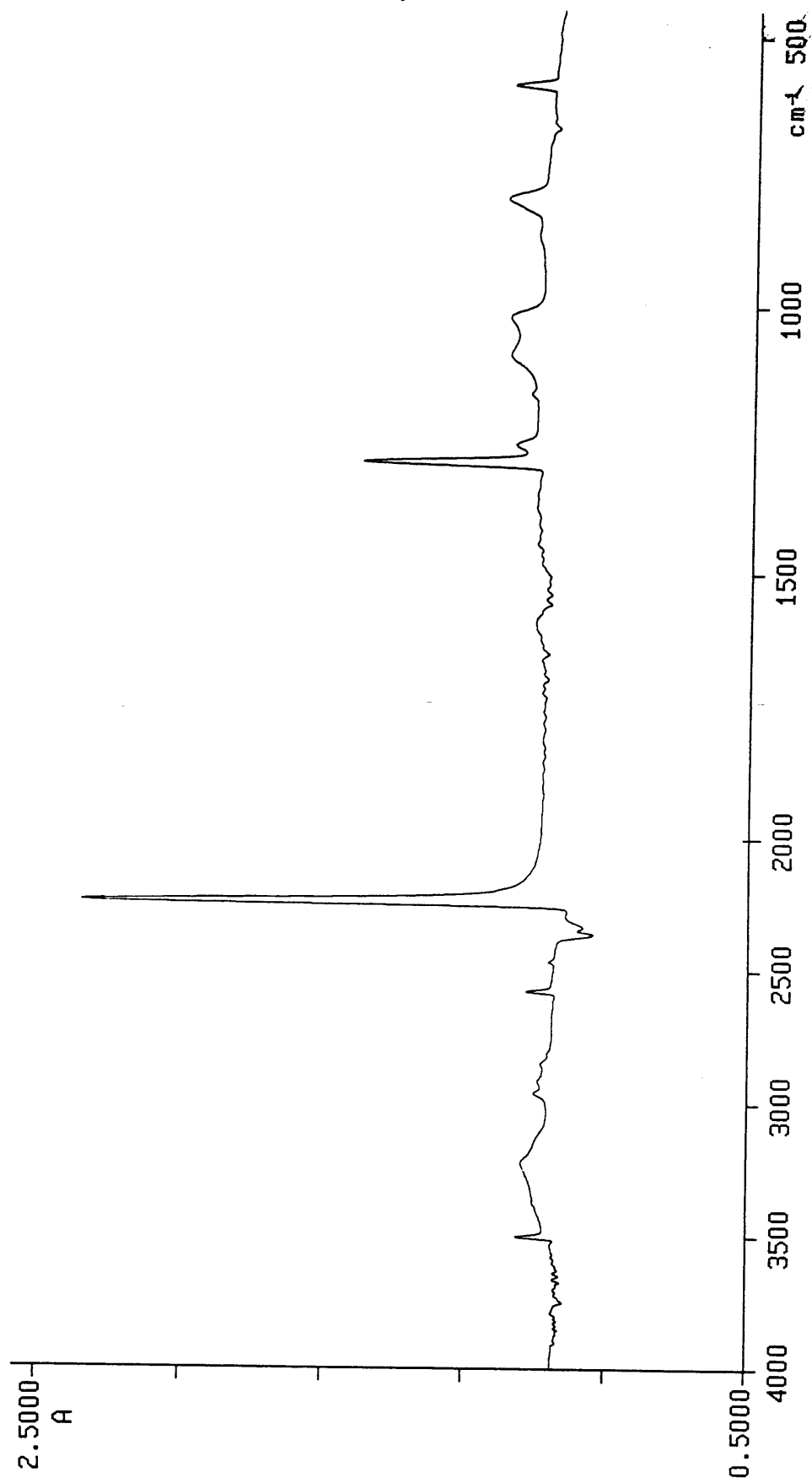


Figure 4.12 IR spectrum of solid N_2O .

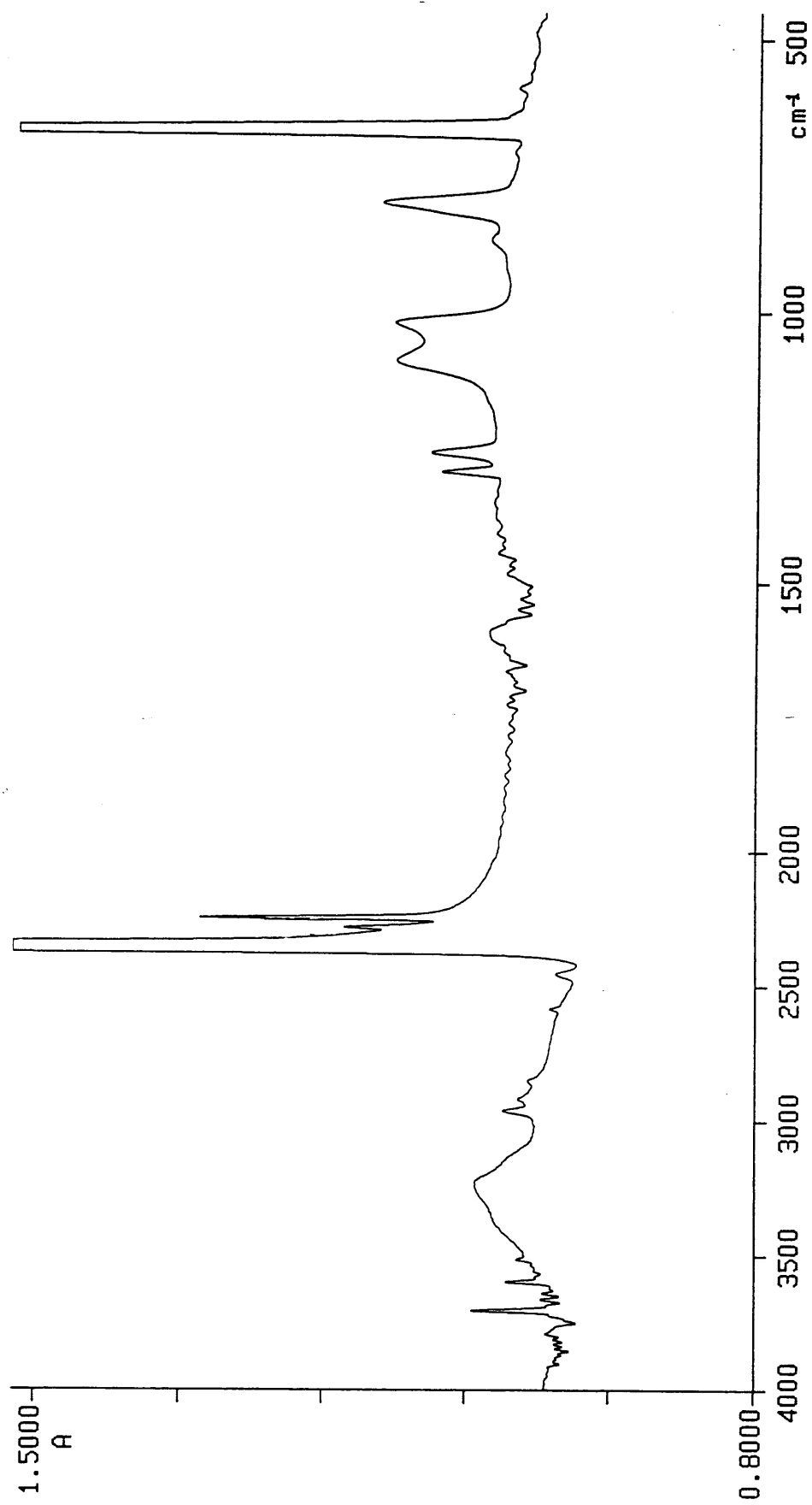


Figure 4.13 IR spectrum of N_2O isolated in CO_2 matrix.

with a medium intensity at 1294 cm^{-1} and a very weak one at 1260 cm^{-1} . The mean of these two lines is red shifted from the gas phase position by 8 cm^{-1} . This band is assigned to the ν_1 absorption. The third line has a low intensity and it is observed at 589 cm^{-1} showing no frequency shift from the gas phase position. This is assigned to the ν_2 absorption.

Table 4.12 IR frequencies^a of N_2O

Mode	Gas ^b	Solid ^c	Matrix-isolated	
			CO_2 matrix ^c	N_2 matrix ^b
ν_2	589	589	589	589
$2\nu_2$	1168	1165	1167	1167
ν_1	1285	1294	1296	1291
		1260	1259	
ν_3	2224	2246	2247	2236
$2\nu_1$	2563	2578	2584	2576

^a All frequencies in cm^{-1} .

^b See reference 21.

^c This work (at 77 K).

Table 4.13 Analysis of gaseous and solid N_2O spectra^a

Mode	Gas ^b	Solid ^c	Frequency shift ^d	Splitting
ν_2	589	589	0	
$2\nu_2$	1168	1165	-3	
ν_1	1285	1294	-8	34
		1260		
ν_3	2224	2246	+22	
$2\nu_1$	2563	2578	+15	

^a All frequencies in cm^{-1} .

^b See reference 21.

^c This work (at 77 K).

^d Average of bands is used for the ν shift calculation.

Table 4.14 Analysis of gaseous and matrix-isolated N₂O spectra^a

Mode	Gas ^b	ν	CO ₂ matrix ^c ν shift ^d	Splitting	ν	N ₂ matrix ^b ν shift	Splitting
ν_2	589	589	0		589	0	
$2\nu_2$	1168	1167	-1		1167	-1	
ν_1	1285	1296 1259	-8	37	1291	+6	
ν_3	2224	2247	+23		2236	+12	
$2\nu_1$	2563	2584	+21		2576	+13	

^a All frequencies in cm⁻¹.^b See reference 21.^c This work (at 77 K).^d Average of bands is used for the ν shift calculation.

A comparison between the frequencies of the gaseous and the CO₂ matrix-isolated N₂O is given in Table 4.14 along with the frequency shifts and the splittings. The frequency of ν_2 does not show any shift from the gas phase position. In the ν_1 band, two lines of almost the same intensity are observed at 1296 and 1259 cm⁻¹. The mean position of these two lines shows a red shift of about 8 cm⁻¹ from the gas phase value and the lines are separated by 37 cm⁻¹. The nitrogen matrix, on the other hand, caused a blue shift of 6 cm⁻¹ with no splitting. The ν_3 band is shown as a very sharp line at 2247 cm⁻¹ and it is well-resolved from the ¹³CO₂ absorption at 2280 cm⁻¹ as shown in Figure 4.14 and therefore it has been selected as the suitable feature in the calibration procedure (see Section 4.3). The line is blue shifted by 23 cm⁻¹ from the gas phase position comparing to a blue shift of 12 cm⁻¹ in the nitrogen matrix. This finding suggests a rather stronger interaction between N₂O and the CO₂ matrix than between N₂O and the N₂ matrix.

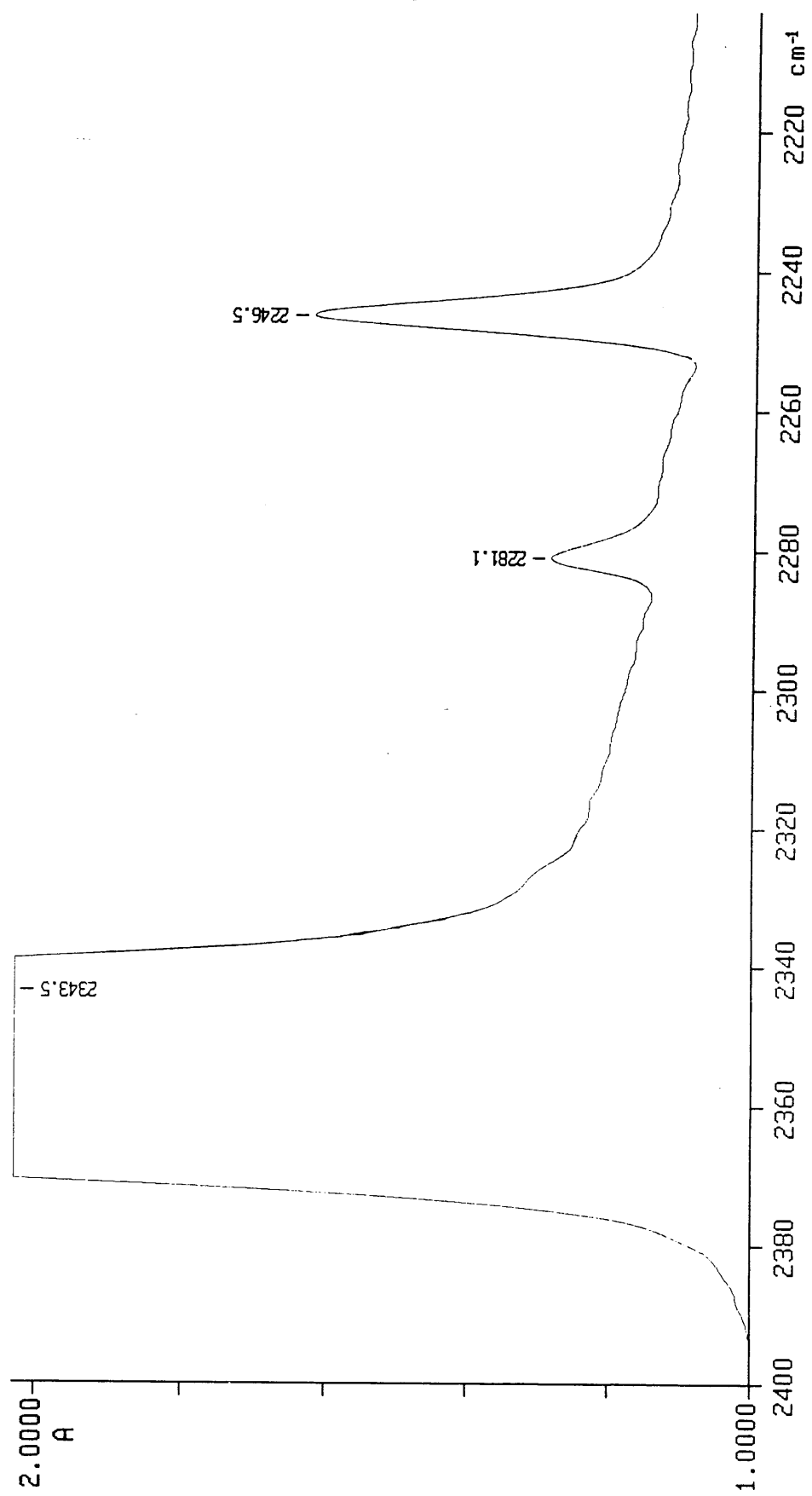


Figure 4.14 IR spectrum showing the N₂O absorption at 2247 cm⁻¹ resolved from the ¹³CO₂ absorption at 2280 cm⁻¹.

4.2.7 SO₂

The infrared spectra of the ³²S, ³⁴S, ¹⁶O, ¹⁸O isotopic species of SO₂ trapped in solid krypton matrices at 20 K have been reported.²² Under conditions of medium resolution ($\sim 0.8\text{ cm}^{-1}$), single bands are observed in each of the spectral regions which correspond to the three vibrational modes. The infrared spectra of matrix isolated SO₂ and NO₂ under conditions of higher resolution (0.3 cm^{-1}) reveal some interesting features in the asymmetric stretching mode ν_3 . These features are discussed in terms of a hindered rotation in the solid krypton matrix.

The matrix spectrum of ³²S¹⁶O₂ corresponded closely to the observed gas-phase spectrum;²³ and it showed no unusual features under these conditions except some indication of high-frequency shoulders on the absorptions in the region between 1290 and 1350 cm^{-1} .

An interesting characteristic of the ν_3 absorption is its temperature dependence.²⁴ Whereas the ν_1 and ν_2 absorptions show only some broadening on temperature cycling of the matrix between 20 and 38 K, the effect on ν_3 is much more dramatic. With increasing temperature, the intensity of the higher-frequency band of the doublet decreases whereas the low-frequency band is temperature insensitive. On decreasing the temperature to 20 K the intensity of the high-frequency band of the doublet is restored to its original value.

In the current work, solid SO₂ and SO₂ isolated in CO₂ matrix (both at 77 K) were studied. The IR spectra of these two phases are shown in Figures 4.15 and 4.16. The IR frequencies of gas, solid and CO₂ matrix-isolated SO₂ are given in Table 4.15. The values of Herzberg²⁵ for gas phase SO₂ are used for comparison. A comparison between the fundamental frequencies of gaseous and solid SO₂ is given in Table 4.16

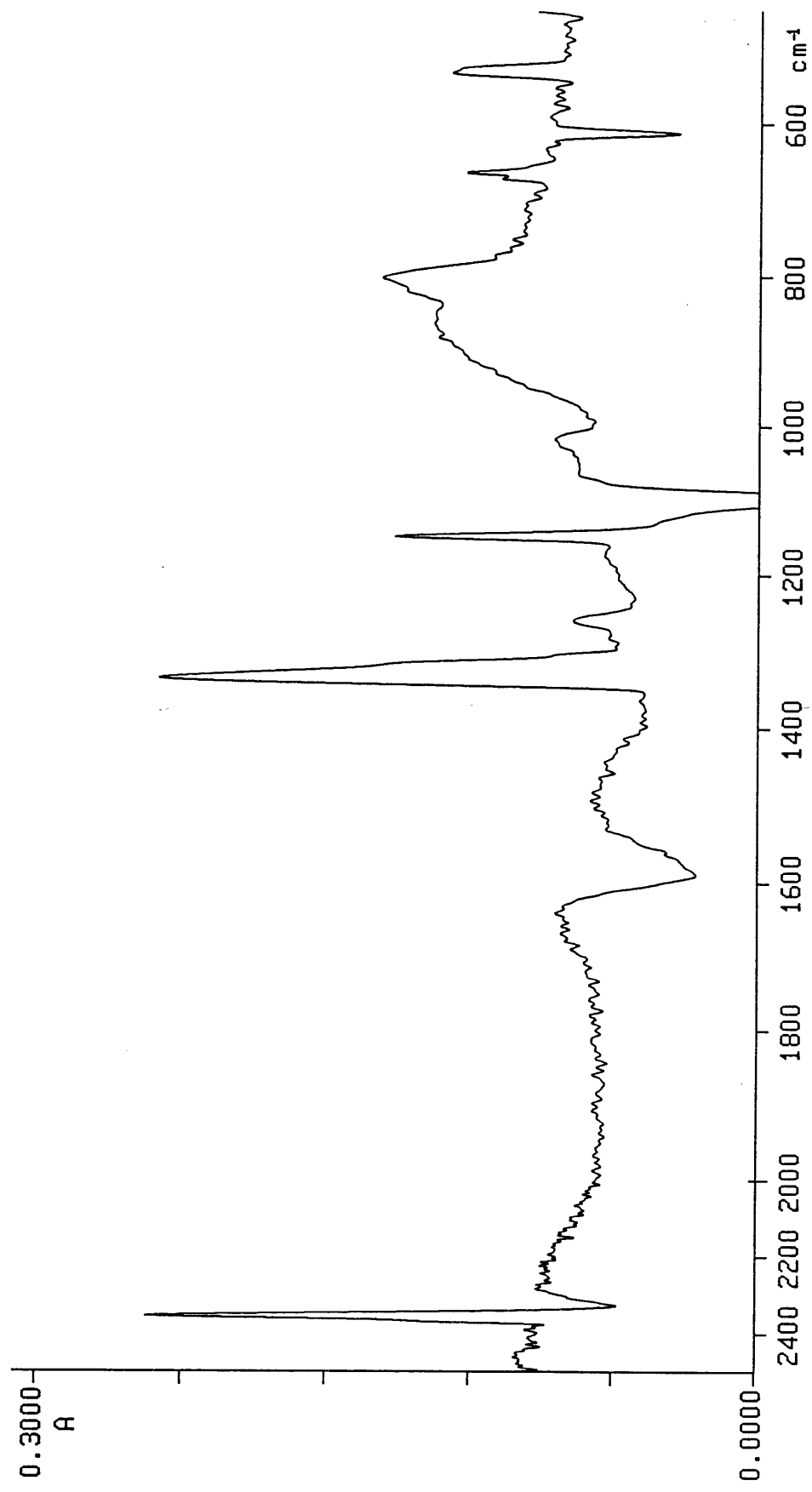


Figure 4.15 IR spectrum of solid SO_2 .

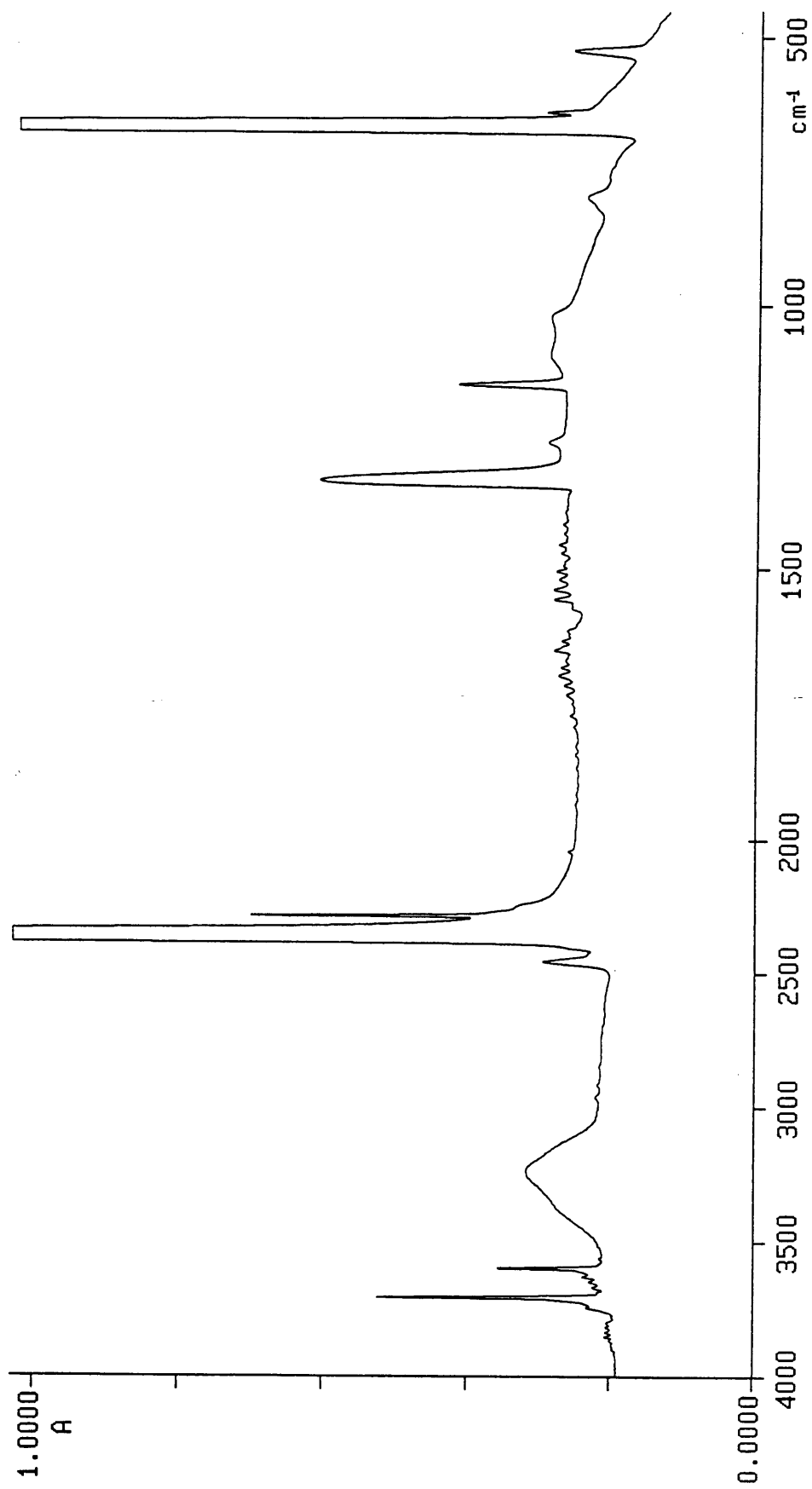


Figure 4.16 IR spectrum of SO₂ isolated in CO₂ matrix.

Table 4.15 IR frequencies^a of SO₂

<u>Mode</u>	<u>Gas</u> ^b	<u>Solid</u> ^c	<u>CO₂ matrix</u> ^c
ν_1	1151	1147 (D) 1139 (D)	1152 (M)
ν_2	518	531 (D) 525 (D)	530 (D) 522 (M)
ν_3	1362	1333 (D) 1316 (D)	1347 (M) 1340 (M) 1321 (D)

^a All frequencies in cm⁻¹; D = Dimer, M = Monomer^b See reference 25.^c This work (at 77 K).**Table 4.16** Analysis of gaseous and solid SO₂ spectra^a

<u>Mode</u>	<u>Gas</u> ^b	<u>Solid</u> ^c	<u>ν shift</u>
ν_1	1151	1147 (D) 1139 (D)	-8
ν_2	518	531 (D) 525 (D)	+10
ν_3	1362	1333 (D) 1316 (D)	-37.5

^a All frequencies in cm⁻¹; D = Dimer, M = Monomer^b See reference 25.^c This work (at 77 K).**Table 4.17** Analysis of gaseous, and CO₂ matrix isolated SO₂ spectra^a

<u>Mode</u>	<u>Gas</u> ^b	<u>CO₂ matrix</u> ^c	<u>ν shift</u>
ν_1	1151	1152 (M)	+1
ν_2	518	530 (D) 522 (M)	+12 +4
ν_3	1362	1347 (M) 1340 (M) 1321 (D)	-18.5 -41

^a All frequencies in cm⁻¹; D = Dimer, M = Monomer^b See reference 25.^c This work (at 77 K).

along with the frequency shifts. A similar comparison between the frequencies of the gas phase and the CO₂ matrix-isolated SO₂ is given in Table 4.17. In the IR spectrum of the solid SO₂, there is a well defined band observed as a sharp peak at 1147 cm⁻¹ with a shoulder at about 1139 cm⁻¹. These are assigned to the ν_1 absorption of the SO₂ dimer by analogy to Nord's assignment.²⁴ The mean of these two absorptions is red shifted from the gas phase position by 8 cm⁻¹. This band is observed in the CO₂ matrix-isolated SO₂ spectrum at 1152 cm⁻¹ with a blue shift of only 1 cm⁻¹ from the gas phase position and is assigned to monomeric SO₂.

Two absorptions are observed in the spectrum of solid SO₂ at 531 and 525 cm⁻¹. The mean of these two absorptions is blue shifted by 10 cm⁻¹ from the gas phase position. These are assigned to the ν_2 absorption of the SO₂ dimer. These absorptions are observed in the CO₂ matrix-isolated spectrum at 530 and 522 cm⁻¹. The band at 530 cm⁻¹ is assigned to the dimeric species of SO₂, while the band at 522 cm⁻¹ is assigned to the monomeric species. The band at 522 cm⁻¹ is blue shifted by 4 cm⁻¹ from the gas phase position.

In the ν_3 region, a strong absorption is observed for solid SO₂ at 1333 cm⁻¹ with a shoulder at about 1316 cm⁻¹. The mean of these two absorptions is red shifted by 38 cm⁻¹ from the gas phase position. Both absorptions are assigned to the dimeric species of SO₂. In the CO₂ matrix-isolated spectrum, on the other hand, three absorptions are observed. The two absorptions at 1347 and 1340 cm⁻¹ are assigned to monomeric SO₂, while the band at 1321 cm⁻¹ is assigned to dimeric SO₂. The mean of the two absorptions assigned to the monomer is red shifted by 18.5 cm⁻¹ from the gas phase position.

In the regions of all three fundamental vibrations of SO₂, one band is observed in the gas phase and is assigned to the monomeric form. In the solid phase, two bands

are observed in each region and are assigned to dimeric SO_2 . In the CO_2 matrix-isolated SO_2 , bands in each region are assigned either to monomeric or to dimeric species, indicating that some SO_2 molecules are isolated by the CO_2 matrix and show similarities to the gas phase, while other molecules are not isolated and are associated to form dimers as in the solid phase.

The two molecules in the SO_2 dimer are inequivalent, giving rise to two bands in each fundamental region in the solid phase.²⁴ Therefore, two alternative structures have been suggested for the SO_2 dimer as shown in Figure 4.17. The first structure (a) has a linear S-O...S bond with one of the C_2 axes along the bond. It is applicable to a case where the ν_1 and ν_2 dimer splits are predominantly due to coupling. In the second structure (b), the C_2 axes are parallel and in one plane. There is a slight ($\sim 15^\circ$) deviation from linearity in the S-O...S bond. This structure is reasonable if the dimer splittings are essentially intrinsic.

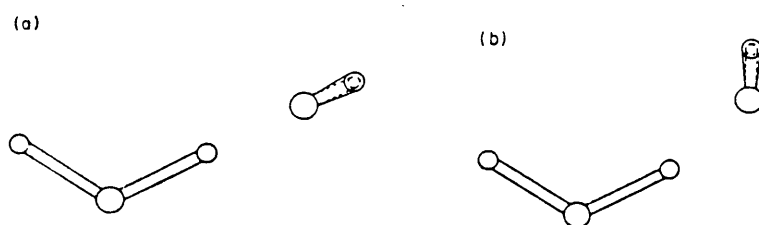


Figure 4.17: Two possible structures for the sulfur dioxide dimer.

Sulfur dioxide has been investigated in cryogenic matrices by several authors.^{22,26-28} The IR frequencies of SO_2 in N_2 , Ar, Kr, Xe, and CO_2 matrices are listed in Table 4.18 for comparison. Only CO_2 and Ar matrices show multiple bands in each region of SO_2 spectrum. As discussed above, these are not considered as line splittings caused by the matrix, but as absorptions of different species of the SO_2 , either

monomeric or dimeric. In general, the frequency shifts among the different matrices range between 8 and 34 cm^{-1} .

Table 4.18 IR frequencies^a of sulphur dioxide in nitrogen, argon, krypton, xenon, and carbon dioxide matrices

	<u>N₂</u> ^b	<u>Ar</u> ^b	<u>Kr</u> ^b	<u>Xe</u> ^b	<u>CO₂</u> ^c
ν_1	1153	1147 1152	1150	1145	1152
ν_2	521	517 520	519	517	530 522
ν_3	1352	1351 1355	1351	1345	1347 1340 1321

^a All frequencies in cm^{-1}

^b See reference 28.

^c This work (at 77 K).

4.2.8 Ethylene

Ethylene is studied in this work as the simplest example of an olefine to analyse its absorptions in CO₂ matrix. In some experiments, ozone was mixed with ethylene in CO₂ matrix for photochemical study (see Section 7.2.4). The IR spectrum of CO₂ matrix-isolated ethylene is shown in Figure 4.18. The fundamental frequencies of the gas-phase, solid and CO₂ matrix-isolated ethylene is given in Table 4.19. Hawkins's gas phase values²⁹ and their assignments are used for comparison. A comparison between the fundamental frequencies of the gaseous and the solid ethylene is given in Table 4.20 with the frequency shifts. A similar comparison between the frequencies of the gas phase and the CO₂ matrix-isolated ethylene is given in Table 4.21. CO₂ matrix shows no splittings in any of the absorptions. The broad peaks centred around 1642 cm^{-1} in the IR

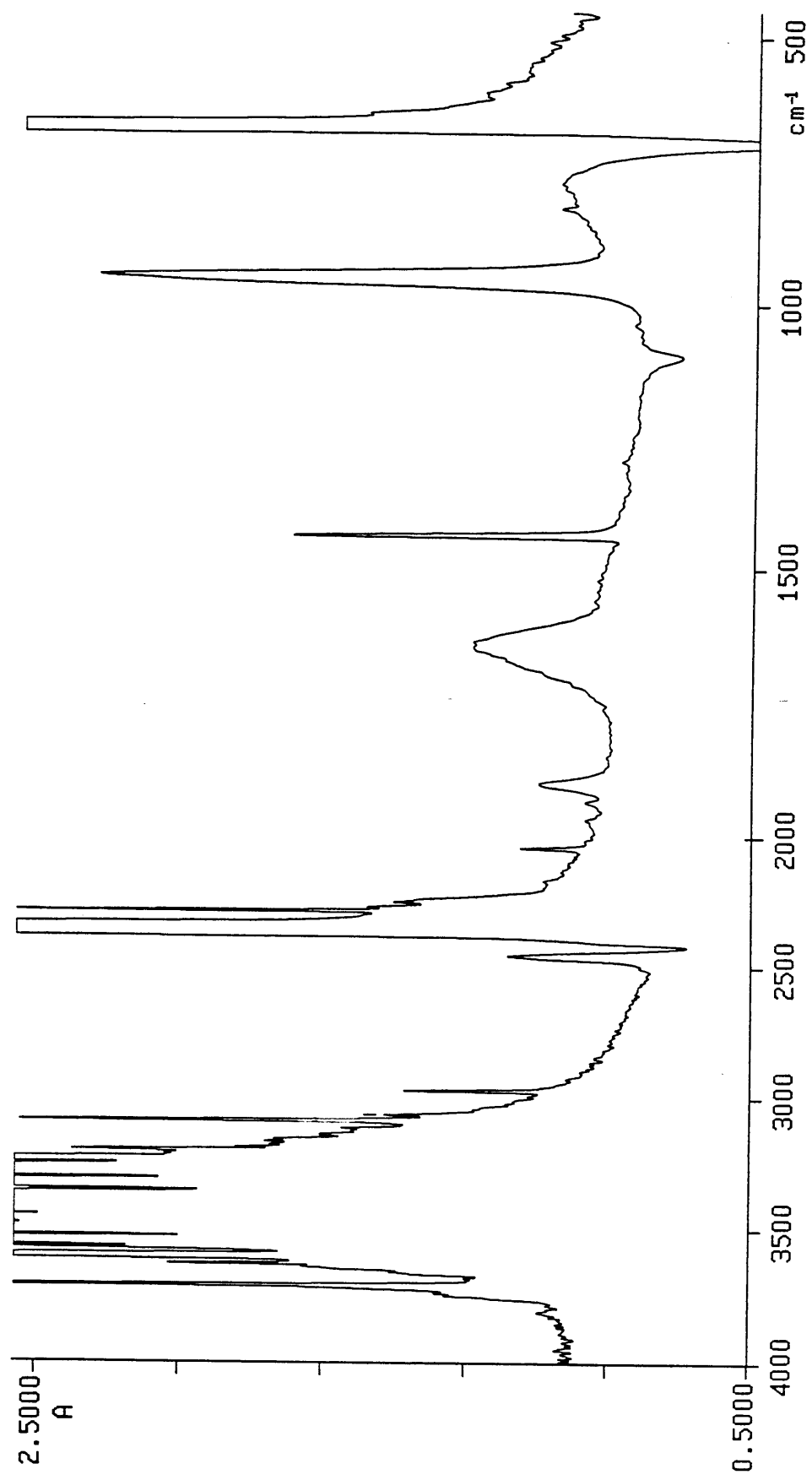


Figure 4.18 IR spectrum of ethylene isolated in CO₂ matrix.

Table 4.19 IR frequencies^a of Ethylene

<u>Mode</u>	<u>Symmetry</u>	<u>Approx.</u> <u>Description</u>	<u>Gas^b</u>	<u>Solid^b</u>	<u>Solid^c</u>	<u>Monomer^b</u> <u>Ar matrix</u>	<u>Dimer^b</u> <u>Ar matrix</u>	<u>CO₂ matrix^c</u>
ν_9	B_{2u}	$\nu_{as}(CH_2)$ _d	3105	3089	3105	3112	3097	3110 ^e
$\nu_2+\nu_{12}$	B_{3u}		3099	3067	3087	3083	3072	3065
ν_{11}	B_{3u}	$\nu_{sym}(CH_2)$	2989	2974	2972	2995	2982	2972
ν_{12}	B_{3u}	CH_2 sciss.	1444	1436	1438	1440	1437	1437
ν_7	B_{2u}	$\omega(CH_2)$	949	951/942	947	946	946	943
ν_{10}	B_{2u}	$\rho(CH_2)$	826	820	821	831	824	820

^a All frequencies in cm^{-1}

^b See reference 29

^c This work (77 K)

^d Combination mode

^e Tentative assignment: band partly obscured by intense ice absorption.

spectrum of solid ethylene and 1635 cm^{-1} in the IR spectrum of ethylene in a CO_2 matrix almost certainly result from impurities of ice in the sample.

Table 4.20 Analysis of gaseous and solid ethylene spectra^a

Mode	Gas ^b	Solid ^c	ν shift
ν_9	3105	3105	0
ν_{11}	2989	2972	-17
ν_{12}	1444	1438	-6
ν_7	949	947	-2
ν_{10}	826	821	-5

^a All frequencies in cm^{-1} .

^b See reference 29.

^c This work (at 77 K).

Table 4.21 Analysis of gaseous and CO_2 matrix isolated ethylene spectra^a

Mode	Gas ^b	CO_2 matrix ^c	ν shift
ν_9	3105	3110 ^d	+5
ν_{11}	2989	2972	-17
ν_{12}	1444	1437	-7
ν_7	949	943	-6
ν_{10}	826	820	-6

^a All frequencies in cm^{-1} .

^b See reference 29.

^c This work (at 77 K).

^d Tentative assignment; band partly observed by intense ice absorption.

The frequencies of combination modes of solid and CO_2 matrix-isolated ethylene are listed in Table 4.22 with the gas phase values for comparison.

There have been previous reports of the IR spectra of ethylene isolated in noble gas matrices^{30,31} although the spectroscopic results are not discussed in detail, and there are complications, especially in the spectrum of ethylene isolated in argon matrices, which have never been fully explained. It is therefore not straightforward to compare the results from CO_2 matrices reported here with similar results from more conventional matrices.

Table 4.22 Comparison between the combination frequencies of gaseous, solid and matrix isolated ethylene spectra

Mode	Gas ^b	Solid ^c	ν Shift ^d	CO ₂ matrix ^c	ν Shift ^d
$\nu_3 + \nu_{12}$	3077	3064	-13	3065	-12
$\nu_6 + \nu_{10}$	2053	2039	-14	2040	-13
$\nu_7 + \nu_8$	1889	1899	+10	1898	+9

^a All frequencies in cm⁻¹.

^b See reference 29.

^c This work (at 77 K).

^d ν shift from gas phase

4.3 Calibration

A suitable spectral line for each pollutant was chosen for data analysis. For N₂O, the line at about 2247 cm⁻¹ assigned to the ν_3 vibration was chosen as the suitable feature. The C=O stretch vibrations at about 1717 cm⁻¹ and 1722 cm⁻¹ were selected for acetone and acetaldehyde, respectively. The double peak (at about 1262 and 1227 cm⁻¹) assigned to the C-O stretch was chosen as a feature for formic acid since the double peak assigned to the C=O stretch overlaps with a water absorption. The C-O stretch at about 1307 cm⁻¹ was selected for acetic acid for the same reason as for formic acid. The band around 1333 cm⁻¹ was selected for SO₂ calibration and the CH bending vibration around 945 cm⁻¹ was chosen as the suitable feature for ethylene. IR spectra were obtained for each mixture and the peak area of pollutant and that of CO₂ were obtained and the ratio between them were calculated. Tables 4.23-4.29 show the spectral data for acetone, acetaldehyde, formic acid, acetic acid, N₂O, SO₂ and ethylene. The pollutant/CO₂ peak area ratios were calculated for different concentrations of the pollutant and listed in the table as ratio 1. The experiment was repeated using mixtures of the same concentrations and the peak area ratios were calculated and listed in the

table as ratio 2. The average ratio was calculated and used for the calibration curves. The calibration curves were constructed for each pollutant using absorption data. It is assumed that Beer's law applies; i.e. that $A = \epsilon cl$ where A is the absorbance, ϵ the absorbtivity, c the concentration of the absorbant, and l its thickness (path length). Since any measurement of the path length l is impossible, the data are expressed in relative absorption of the pollutant to CO_2 . The absorption of one species is assumed to be not affected by the presence of other materials, whether they absorb or not, according to the law of additivity. By using this method, the total amount of the sample sprayed on the spectroscopic window is not required to be fixed for all the samples. Using one of the sample mixtures, the need of having the same amount of the sample each time was tested. 50 Torr of the sample was sprayed on the spectroscopic window and a spectrum was obtained for that sample. The peak area ratio was calculated to be 1.12. Another 50 Torr of the same sample was sprayed again to get a thicker film and a spectrum was obtained for the second sample. The peak area ratio for 100 Torr of the sample was 1.10. These two values are considered to be within experimental error. The best line fit was plotted for each pollutant as shown in Figures 4.19-4.25 at the end of this section. The plot in the case of N_2O was linear with a slope of 0.96 but it loses linearity below 1% because of the difficulty of controlling the pressure at low range. N_2O was detected to a limit of 0.01% in CO_2 . Since CO_2 is present in air at a concentration of about 0.0325% by volume,¹ a minimum of 0.01% N_2O in CO_2 was measured which is equivalent to about 32.5 ppb of N_2O in air. Acetone and acetaldehyde, on the other hand, were measured to a level of 1% in CO_2 or 3.3 ppm in air. Formic acid gave a straight line with a slope of 0.34 and was detected to a limit of 0.7% in CO_2 or 2.3 ppm in air, while acetic acid was linear with a slope of 0.33 and has a detection limit of 1% in CO_2 which is equivalent to 3.3 ppm in air. SO_2 gave a straight line with a slope of

0.20 and was detected to a limit of 0.1% in CO₂ which is equivalent to 325 ppb in air and ethylene also gave a straight line with a detection limit of 1% in CO₂ or 3.3 ppm in air.

Table 4.23 Spectral data for acetone

<u>% acetone</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
1.1	0.37	0.30	0.34
2.6	0.64	0.73	0.69
4.4	1.05	1.34	1.19
6.9	1.60	1.91	1.75
9.1	2.65	2.41	2.53

Table 4.24 Spectral data for acetaldehyde

<u>% aldehyde</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
0.95	0.69	0.51	0.60
2.3	1.11	1.27	1.19
5.0	2.03	1.83	1.92
7.1	3.62	3.18	3.40
11.1	5.94	5.29	5.61

Table 4.25 Spectral data for formic acid

<u>% F. A.</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
0.5	0.17	0.17	0.17
1	0.33	0.34	0.34
3.5	1.25	1.19	1.22
5	1.84	1.62	1.73
7	2.30	2.39	2.35
10	3.38	3.36	3.37
24	7.83	8.14	7.99
48	16.74	16.29	16.52
62	20.53	21.06	20.80

Table 4.26 Spectral data for acetic acid

<u>% A. A.</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
1	0.413	0.396	0.405
2	0.683	0.610	0.647
5	1.470	1.583	1.527
7.5	2.432	2.493	2.463
10	3.271	3.441	3.356

Table 4.27 Spectral data for N₂O

<u>% N₂O</u>	<u>Ratio 1</u>	<u>ratio 2</u>	<u>ratio 3</u>	<u>Average</u>
0	0	0	0	0
0.01	0.035	0.014	0.078	0.042
0.05	0.123	0.120	0.172	0.138
0.23	0.301	0.298	0.334	0.311
0.6	0.443	0.439	0.470	0.451
1	0.663	0.676	0.652	0.664
2	1.780	1.777	1.797	1.785
5	4.694	4.712	4.702	4.703
10	9.550	9.564	9.559	9.558
25	24.011	23.998	24.003	24.004

Table 4.28 Spectral data for SO₂

<u>% SO₂</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
0.1	0.049	0.051	0.050
0.5	0.147	0.169	0.158
1.0	0.263	0.247	0.255
1.5	0.472	0.448	0.460
1.75	0.530	0.490	0.510
5.0	0.903	0.839	0.871
10	1.880	2.040	1.960
20	4.120	3.760	3.940

Table 4.29 Spectral data for ethylene

<u>% ethylene</u>	<u>ratio 1</u>	<u>ratio 2</u>	<u>Average</u>
0	0	0	0
1	0.027	0.023	0.025
3.8	0.163	0.203	0.183
8.8	0.639	0.501	0.570
18.2	1.411	0.892	1.152

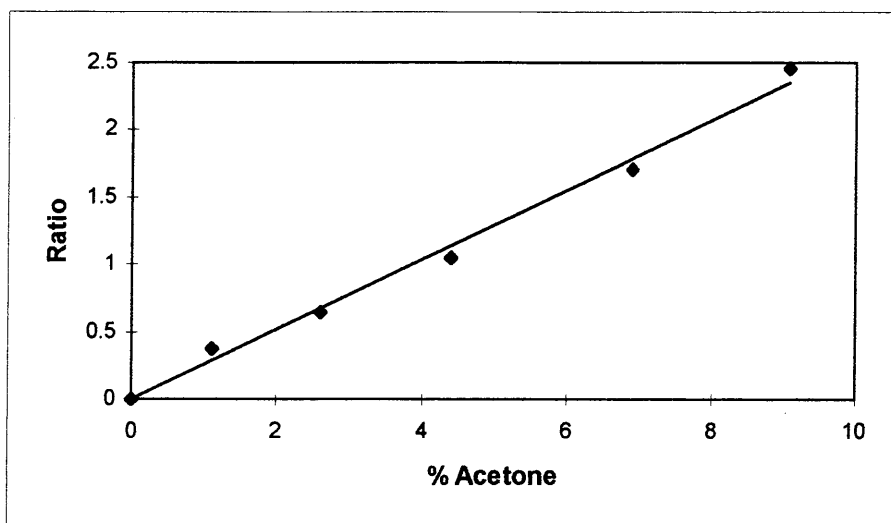


Figure 4.19 Calibration curve of acetone in CO₂ matrix

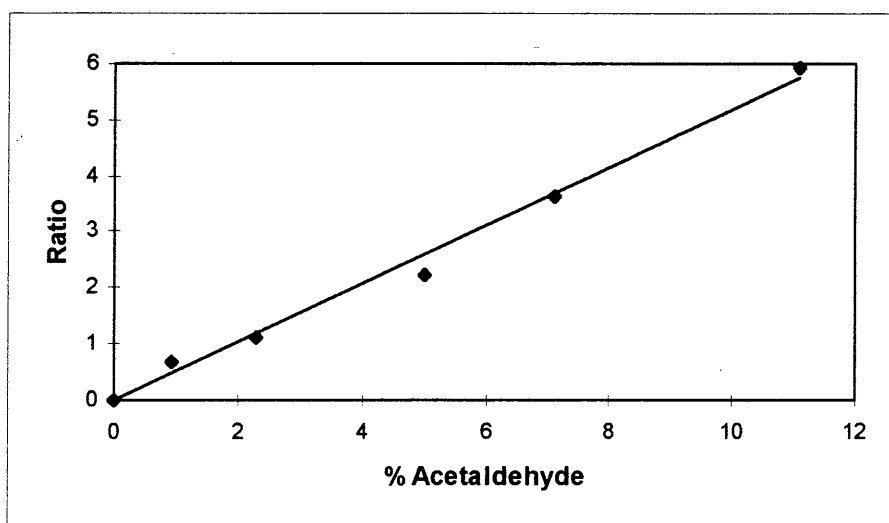


Figure 4.20 Calibration curve of Acetaldehyde in CO₂ matrix.

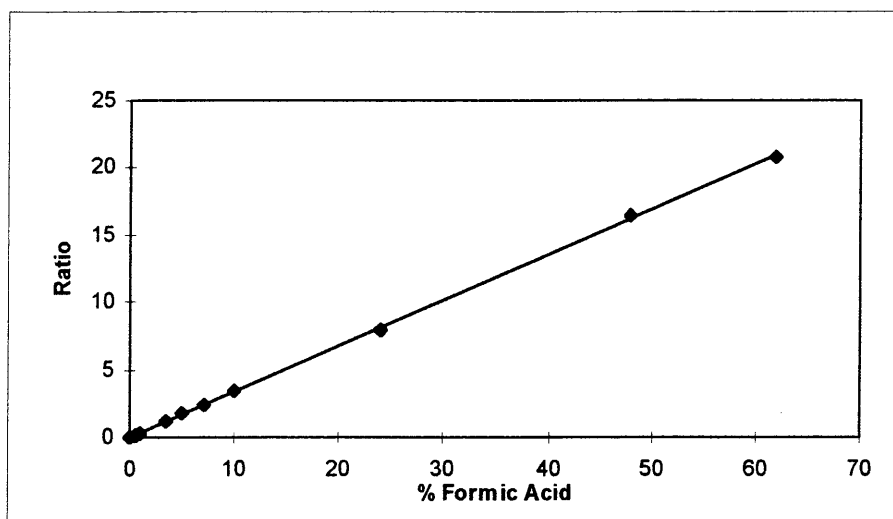


Figure 4.21 Calibration curves of formic acid in CO₂ matrix.

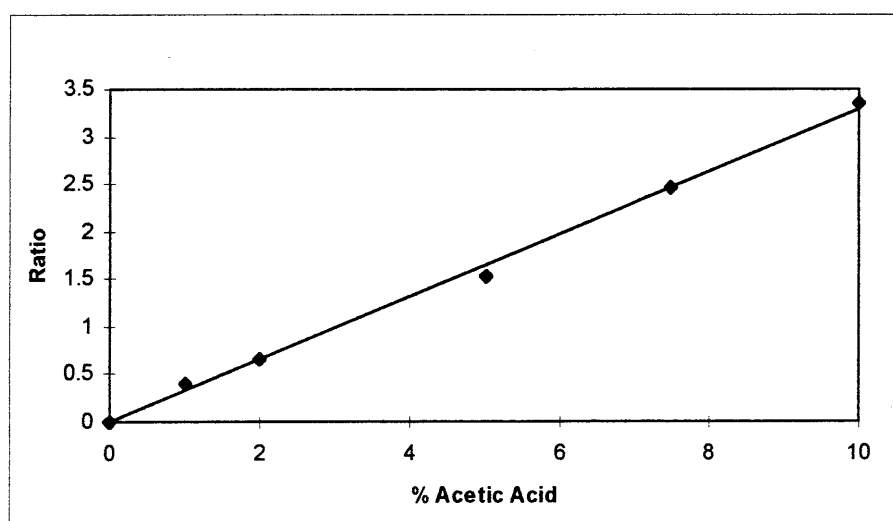


Figure 4.22 Calibration curve of acetic acid in CO₂ matrix.

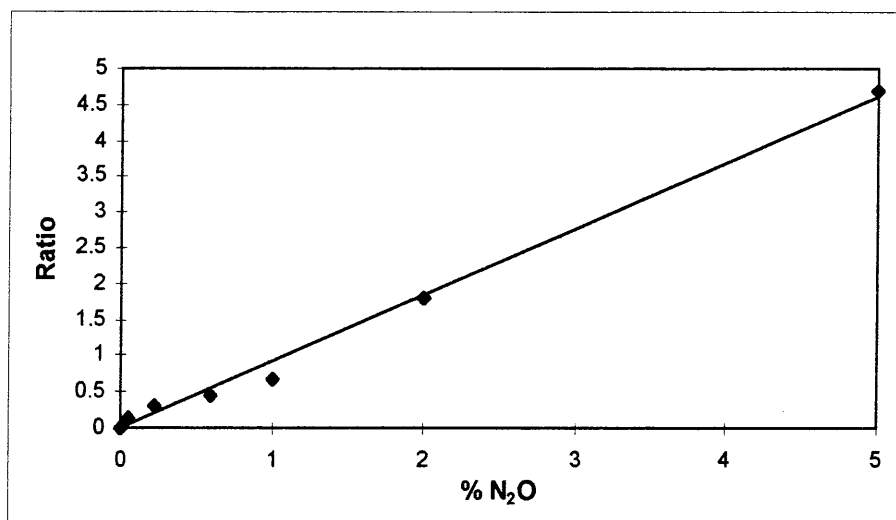


Figure 4.23(a) Calibration curve of N₂O in CO₂ matrix (lower concentrations).

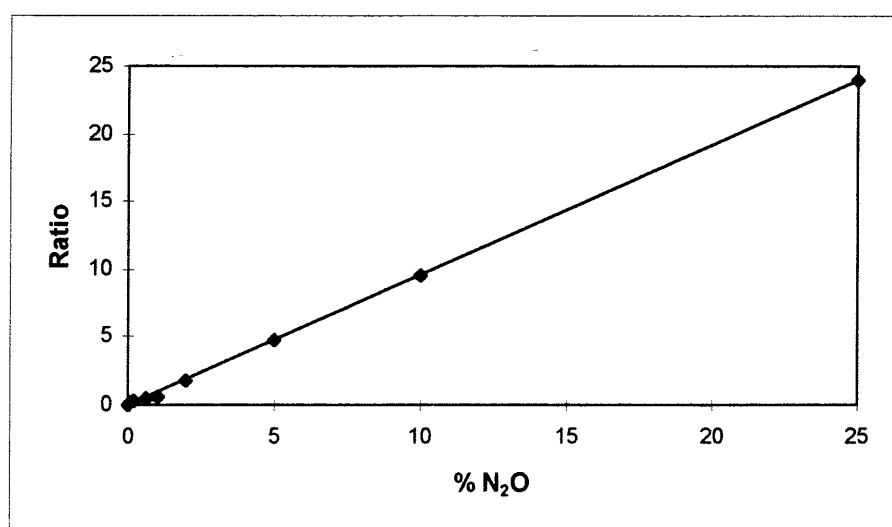


Figure 4.23(b) Calibration curve of N₂O in CO₂ matrix (higher concentrations).

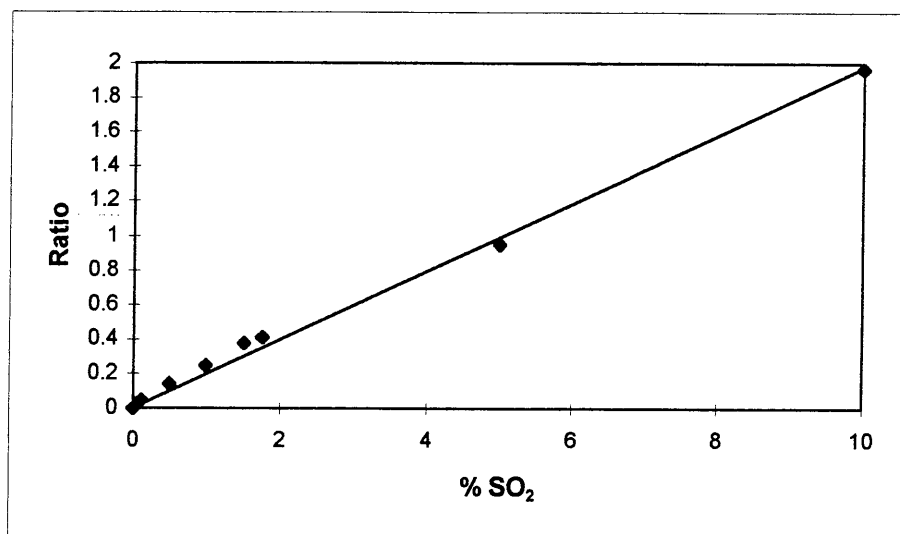


Figure 4.24 Calibration curve of SO₂ in CO₂ matrix.

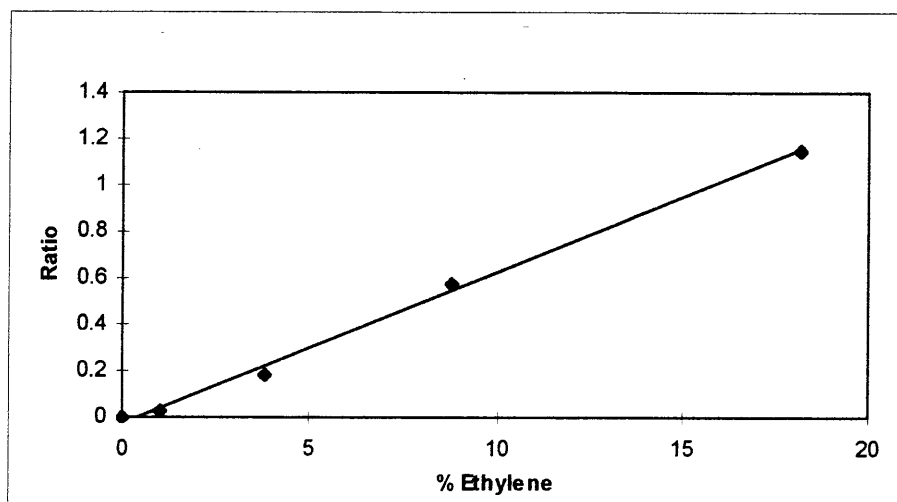


Figure 4.25 Calibration curve of ethylene in CO₂.

The spectral measurement was one of the important steps in the whole procedure that could be a great source of errors. Background spectra should be taken for the empty cell and subtracted from the sample spectra to get rid of all the extra lines that occurred due to the presence of CO₂ and water vapour in the atmosphere. Base line correction was also carried out to get better intensity measurements. Careful deposition of thicker matrices might allow lower concentrations of pollutants to be detected.

4.4 Effect of water

Water vapour absorbs at 3756, 3652 and 1596 cm⁻¹,³² whereas the solid formed on condensation at very low temperatures has an extremely intense, broad band centered at approximately 3250 cm⁻¹, a broad band of moderate intensity at 810 cm⁻¹ and a fairly weak, broad band at approximately 1600 cm⁻¹.³³ Matrix isolation experiments were performed using mixtures of water in CO₂ ranging from 1-10%. In all of the experiments bands appeared at about 3387 and 1652 cm⁻¹.

In the designing of the portable vacuum line, water was considered since it has some absorption peaks which overlap with the analyte absorption around 1500 cm⁻¹ and also because of the possibility of hydrogen bonding between water and other reagents. The effect of water on the absorption spectra was studied on formic acid. Water may form a hydrogen bond with the carbonyl oxygen of the formic acid and decrease the double bond characteristic which leads to a lowering in the carbonyl frequency. Different amounts of water were added to mixtures of 6% formic acid in CO₂. For each mixture the IR spectrum was obtained and the peak area ratio of formic acid to CO₂ was calculated and is listed in Table 4.30. The ratios were plotted against the concentration of water as shown in Figure 4.26. The plot was almost a flat line (a straight line with a

slope of zero) which implies that the presence of water in the sample mixture does not have critical effect on the absorption spectra and, therefore, does not present a problem if present in the sample mixture at low concentrations. The portable apparatus must not be too complicated if it is to be used easily in the field but a low-temperature trap to remove some of the atmospheric water could readily be used.

Table 4.30 Effect of water on absorption spectra of formic acid

<u>% water</u>	<u>F. A. area</u>	<u>CO₂ area</u>	<u>Ratio</u>
0	2.55	1.12	2.28
2	1.40	0.72	1.94
4	1.82	0.85	2.14
6	1.80	0.88	2.05
8	1.15	0.59	1.95

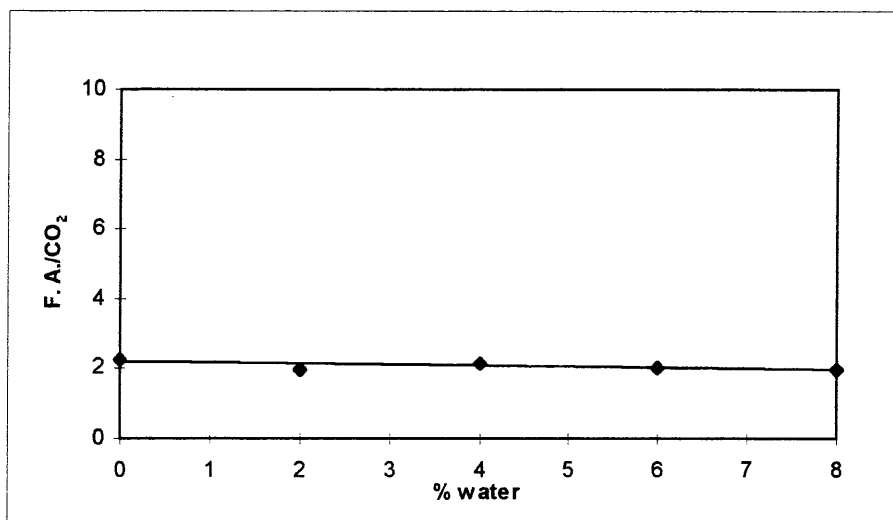


Figure 4.26 Effect of water on the infrared spectra of formic acid in CO₂ matrix.

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5.1 Introduction

In the experiments reported in Chapter 4 the MI-FTIR technique was used to study the IR spectra of some compounds including carbonyl compounds. The technique requires conventional spectrometric instrumentation but uses cryogenic temperatures to affect an unusual method of gas mixture preparation. This results in condensed-phase spectra characterised by relatively sharp absorptions, few in number, occurring at highly reproducible frequencies. Such spectra contrast markedly with normal gas-phase spectra and encourage use of low temperature sample preparation for gas analysis (see Chapter 7).

One cannot discount entirely the possibility that CO₂ matrix could result in new absorptions since it is not totally inert and also the possibility of the presence of some interactions between the compounds and CO₂ matrix, even at high M/A ratio, which could lead to slightly different spectra from those of the gas-phase or even from the spectra of the same compounds isolated in different matrices which have been reported in other studies.

To study the effect of the CO₂ matrix on the IR spectra of the carbonyl compounds, it was thought that the use of deuterated compounds would be informative. Thus the spectra of the deuterated compounds can be compared to those of the light isotopomers. In this chapter, MI-FTIR spectroscopy is applied to some isotopically labeled carbonyl compounds in CO₂ matrices. The method used is essentially the same as that used for the non-labelled compounds. Data for deuterated acetone, acetic acid and formic acid are presented. In particular investigation of carboxylic acids where –OH

groups are replaced by –OD was considered desirable given the possibility that such groups may engage in hydrogen-bonding with the CO₂ matrix.

5.2 Experimental

The infrared spectra of some isotopic derivatives of a range of carbonyl compounds have been studied over the 4000-450 cm⁻¹ region. The compounds are acetone-*d*₆; 99.9 + atom % D, acetic acid-*d*; 98 atom % D, acetic-*d*₃ acid-*d*; 99.5 atom % D and formic-*d* acid-*d*; 99+ atom % D. The compounds were obtained from Aldrich and were used without any further purification.

At the beginning of each experiment, each compound was degassed in a series of freeze-pump-thaw cycles in a high-vacuum line. The vapour of the compound under investigation (X) was mixed in a glass bulb with CO₂ gas in a 1:5 (X/CO₂) ratio and was condensed onto the cold window. The flow of the mixture was controlled by a manually adjusted valve. FTIR absorption spectra were recorded. A single-beam reference spectrum of the cold substrate was recorded before formation of the matrix. This spectrum was then subtracted from all subsequent spectra. Typical spectra were taken at 1 cm⁻¹ resolution with 16 scans averaged per spectrum.

5.3 Spectral analysis

5.3.1 Acetone-*d*₆

CO₂ matrices containing either acetone-*h*₆ or acetone-*d*₆ were prepared, yielding infrared absorption spectra (Figure 5.1) that were similar to those previously reported

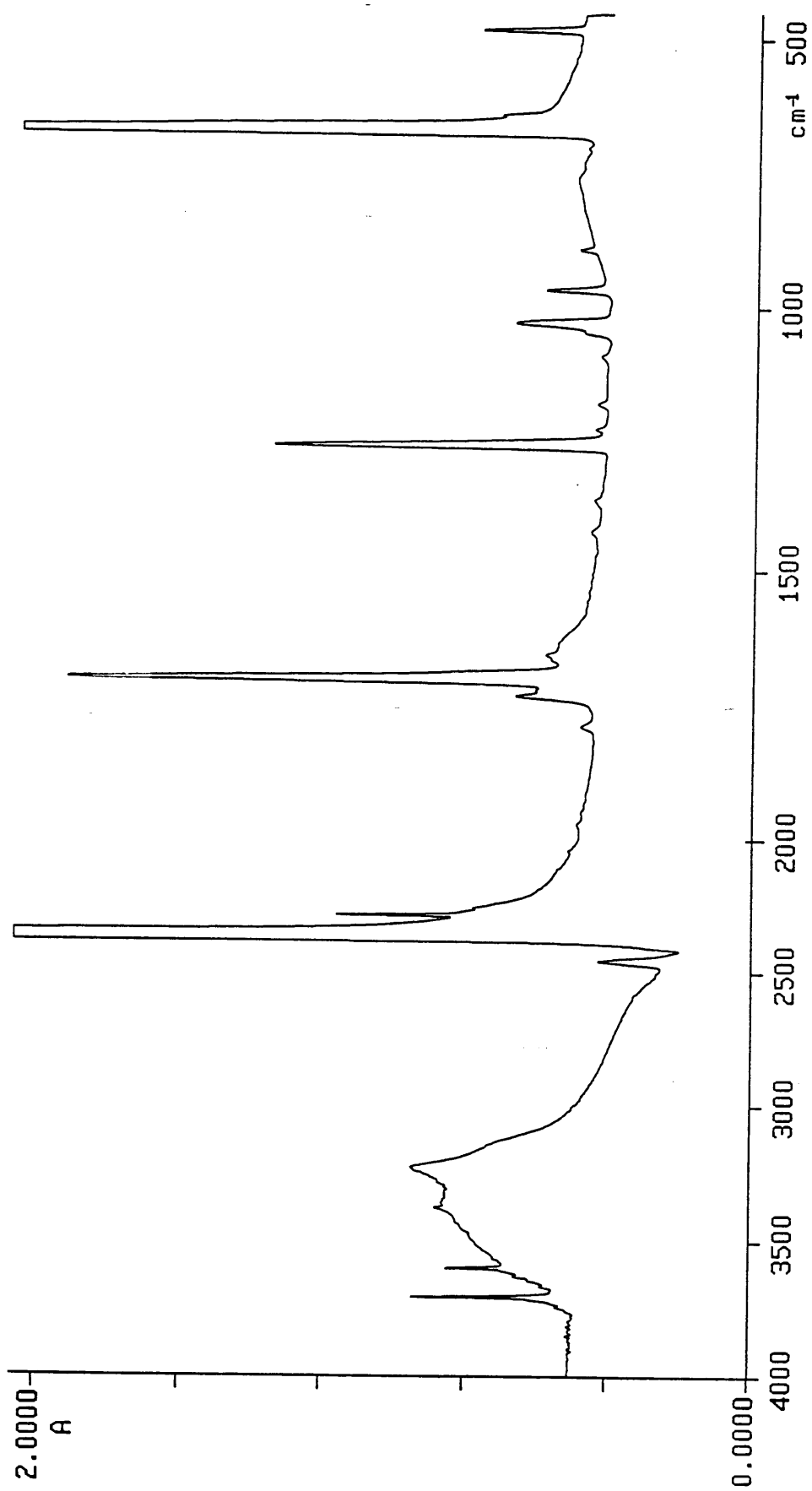


Figure 5.1 IR spectrum of acetone-*d*₆ isolated in CO₂ matrix.

for argon matrices.¹ In Tables 5.1 and 5.2 are summarized the observed fundamental absorptions for acetone-*h*₆ and acetone-*d*₆, respectively, with spectral assignments based upon the work of Dellepiane and Overend.¹ The fundamental absorptions for both gas-phase and CCl₄ solution samples were listed in the tables for comparison. The spectrum of acetone-*h*₆ was as expected for the isolated molecule, showing no significant indication of dimerization in the CO₂ matrix.

Table 5.1 Vibrational spectra and assignments of acetone-*h*₆.^a

<u>Gas^b</u>	<u>Solution^{b,c}</u>	<u>Ar matrix^b</u>	<u>CO₂ matrix^d</u>	<u>Assignment^b</u>
1731	1715	1725	1711.5	ν_3 , C=O str.
1454		1458.5		ν_{21}
		1445		ν_{6+8}
1435	1434	1430	1441	ν_4 , asym. CH ₃ def.
1410	1418	1408	1418.5	ν_{15} asym. CH ₃ def.
1363.5	1359	1363	1366	ν_{16} , sym CH ₃ def.
		1355	1351	ν_5 , sym. CH ₃ def.
1215.5	1218	1217	1233.5	ν_{17} , asym. C-C str.
1090.5	1089	1090	1096.5	ν_{22} , CH ₃ rock. (oop)
891	898	880	843	ν_{18} , CH ₃ rock. (ip)
777	782			ν_7
530	530	530	534.5	ν_{19} , C=O def. (ip)
484	488			ν_{23}

^a All frequencies in cm⁻¹

^b See reference 1

^c Solution in CCl₄

^d This work

One of the basic difficulties in interpreting the IR spectrum of matrix-isolated acetone is that many of the fundamentals are almost degenerate. Acetone has six carbon-hydrogen stretching vibrations in the region of 3000 cm⁻¹, six carbon-hydrogen deformations in the region of 1400 cm⁻¹ and four methyl-rocking vibrations at about 1000 cm⁻¹, and many bands, particularly in the gas-phase infrared spectrum are badly overlapped. The same problem of degeneracy is encountered in the spectrum of acetone-*d*₆. However, in the spectrum of $\alpha\alpha\alpha$ acetone-*d*₃ the degeneracies in the

methyl-group vibrations are partially removed and the problem of overlapping bands is somewhat mitigated.¹

Table 5.2 Vibrational spectra and assignments of acetone-*d*₆.^a

<u>Gas^b</u>	<u>Solution^{b,c}</u>	<u>Ar matrix^b</u>	<u>CO₂ matrix^f</u>	<u>Assignment^b</u>
1732	1707	1738	1701 ^g	ν_3 , C=O str.
1480				$\nu_4+\nu_{23}$
1420	1419		1427	$\nu_5+\nu_{23}$
1370	1361			$\nu_6+\nu_{19}$
			1366	
1241.7	1245	1240	1261	ν_{15}
			1229	
	1196	1196	1181	$\nu_6+\nu_7$
1160	1169	1175		ν_{17+19}
1080	1084	1088	1090.5	ν_4
1050	1046	1050	1044.5	ν_{21}
1035	1032	1035	1027.5	ν_{16}
1004	1001	1001	966	ν_{17}
960	961	963		$\nu_6+\nu_{24}$
887	883	885	891	ν_6 , CD ₃ rock.
689	690 ^d			ν_7
475	480	475	481.5	ν_{19} , C=O def.
405	408.5 ^e			ν_{23}
321	327.5 ^e			ν_8

^a All frequencies in cm⁻¹

^b See reference 1

^c Solution in CCl₄

^d Solution in CS₂

^e Solution in trans-dichloroethylene

^f This work

^g Matrix split band: most intense component at 1701 cm⁻¹.

In CO₂ matrix-isolated acetone, the carbonyl stretching vibration appears as a very intense band at 1711.5 cm⁻¹. CO₂ matrix-isolated acetone-*d*₆, on the other hand, shows a strong band at 1701 cm⁻¹ and a weak (presumably matrix-split) band at 1734 cm⁻¹. The positions of the intense $\nu(\text{C=O})$ absorptions in both isotopomers are closer to the CCl₄ solution value recorded by Overend¹ than to the gas-phase or the argon matrix values. The spectral changes which are produced in solid solutions generally resemble

those that accompany the dissolution of molecules in liquid solvents, but there are several additional effects which arise due to the matrix environment.

A strong band of acetone in CO₂ matrix at 1233.5 cm⁻¹ is assigned to the asymmetric carbon-carbon stretching vibration showing blue shifts of 18 cm⁻¹ from the gas phase position and 15.5 cm⁻¹ from the CCl₄ solution position. The corresponding mode of acetone-*d*₆ in CO₂ matrix is assigned to similar band at 966 cm⁻¹ with red shifts of 38 cm⁻¹ from the gas phase position and 35 cm⁻¹ from the CCl₄ solution position (see Tables 5.1 and 5.2). The behaviour of the asymmetric carbon-carbon stretching frequency in increasing in frequency upon deuteration is understandable as in acetone the methyl deformations fall at higher frequency and in acetone-*d*₆ at lower frequency. Thus the coupling of $\nu(\text{C-C-C})$ and $\delta(\text{CH}_3)$ vibrations is altered in the deuterated isotopomer leading to an increase in $\nu(\text{C-C-C})$. The carbonyl deformation of acetone should be assigned to the intense band at 534.5 cm⁻¹ and that similar intense band at 481.5 cm⁻¹ in acetone-*d*₆ should be similarly assigned. The latter absorption is also closer to the solution absorption. When the molecule is deuterated, the carbonyl deformation frequency is depressed.

The assignment of the methyl deformations in the undeuterated molecule is complicated by the fact that there are two methyl groups and hence six modes to be assigned. The low-temperature infrared spectrum of acetone in a CO₂ matrix shows two barely resolved doublets at 1441 and 1418.5 cm⁻¹ and at 1366 and 1351 cm⁻¹. These can be assigned to CH₃ deformations. Four absorptions were recorded by Overend for acetone in an argon matrix at 1430, 1408, 1363 and 1355 cm⁻¹, while in the gas-phase and solution spectra the fourth absorption was not observed.

An isolated CD₃ group which belongs to the C_{3v} point group is similarly expected to have two deformation frequencies; the symmetric (*A*₁) mode at about 1066

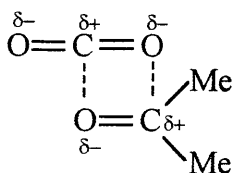
cm^{-1} and the degenerate asymmetric (*E*) mode at about 1039 cm^{-1} .¹ In the IR spectrum of CO_2 matrix-isolated acetone- d_6 , two very weak absorptions appear at 1427 and 1366 cm^{-1} which are very close to the CH_3 deformation modes assigned above and may be assigned to an impurity of the undeuterated isotopomer. There is a sharp, weak line at 1090.5 cm^{-1} which can be assigned to a CD_3 deformation. This was observed by Overend in argon matrix at 1088 cm^{-1} . A sharp peak is observed at 1027.5 cm^{-1} with a shoulder at about 1044.5 cm^{-1} . These can be assigned as other CD_3 deformation frequencies. These were assigned by Overend in argon matrix at 1035 and 1050 cm^{-1} .

Overend has already concluded that the $\nu_{\text{sym}}(\text{C-C-C})$ and $\delta_{\text{sym}}(\text{CH}_3)$ vibration in matrix-isolated acetone are coupled. Similar coupling would account for the abnormally high frequency of $\delta_{\text{sym}}(\text{CD}_3)$ mode (1090.5 cm^{-1} in CO_2 matrix) and provides further evidence that $\delta_{\text{asym}}(\text{CD}_3)$ is coupled to the $\nu_{\text{asym}}(\text{C-C-C})$ (1261 cm^{-1} in a CO_2 matrix). Therefore, as $\nu_{\text{asym}}(\text{C-C-C})$ occurs at an unusually high frequency in a CO_2 matrix, $\nu_{\text{asym}}(\text{CD}_3)$ should be expected to be depressed and to lie at an abnormally low frequency, and, accordingly, this can be assigned to the band at 966 cm^{-1} in the CO_2 matrix.

The CH_3 rocking frequencies in acetone are expected to lie in the region 900 - 1000 cm^{-1} . Not all of the modes are IR active. The band at 1096.5 cm^{-1} in CO_2 matrix-isolated acetone is assigned to the B_2 out-of-plane CH_3 rocking mode (observed by Overend at 1090 cm^{-1} in argon matrix). The other band at 843 cm^{-1} (at 880 cm^{-1} in argon matrix) is assigned to the A in-plane CH_3 rocking mode. The rocking vibrations of the CD_3 group are expected to parallel those of the CH_3 group but to fall at somewhat lower frequencies (between 700 and 850 cm^{-1}). Acetone- d_6 is transparent in this region. There is a very weak band at about 891 cm^{-1} which can be assigned to a CD_3 rocking mode. This was observed by Overend in argon matrix at 885 cm^{-1} .

In conclusion it may be said that there are many similarities between the spectra of acetone and of acetone- d_6 in argon and CO₂ matrices. The principal differences are:

- 1) $\nu_{\text{asym}}(\text{C-C-C})$ lies at a higher frequency and $\delta_{\text{asym}}(\text{CD}_3)$ at lower frequency for acetone- d_6 isolated in CO₂ as compared to the same molecule isolated in argon. This is almost certainly a result of increased coupling.
- 2) $\nu(\text{C=O})$ of acetone in CO₂ has a value much closer to that of acetone in solution than in an argon matrix or in the gas phase. This may imply some interaction with the matrix, e.g., a dipole-dipole interaction between matrix host and guest molecules, which, of course, will not occur in an argon matrix.



Interestingly, for acetone- d_6 a doublet is seen in the $\nu(\text{C=O})$ region with one component at 1734 cm⁻¹ (close to the argon matrix value of 1738 cm⁻¹(1)) and one component at 1701 cm⁻¹ (close to the CCl₄ solution value of 1707 cm⁻¹ (1)). This may suggest the presence of acetone- d_6 molecules with or without a dipole-dipole interaction to the host CO₂ molecules. There are therefore subtle differences between the IR spectrum of acetone when trapped in CO₂ or argon matrices.

In the spectrum reproduced in Figure 5.1, and in other CO₂ matrix spectra, an intense doublet is observed at 3609 and 3716 cm⁻¹. These are combination bands of CO₂ and arise as a result of Fermi resonance between $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$. The IR fundamentals of CO₂ are discussed in detail in section 2.8 while comments on combination modes are given in section 2.6.

5.3.2 Acetic Acid-*d*

The study of the infrared spectrum of acetic acid is complicated by the fact that, even in the vapour phase, acetic acid is a mixture of two species, monomers and dimers, the latter being formed by very strong hydrogen bonding between two monomeric molecules to yield a cyclic structure.² From studies of the effect of temperature on the degree of this association in acetic acid,³ it is found that at 150°C the vapour is nearly completely monomeric and, hence, in order to obtain the infrared spectrum of the monomeric acid with the minimum interference from the dimeric form, it was necessary to study the vapour at this temperature. This has been done by Gillette and Daniels,⁴ who investigated the effect of temperature on the infrared spectrum of acetic acid vapour by obtaining the spectrum at 25° and 144°C, and by Herman and Hofstadter,⁵ who obtained the infrared spectra of acetic acid and acetic acid-*d* vapours at 25° and 144°C, in an investigation upon the strength of the hydrogen bonds in the dimeric acid.

In this investigation, the infrared spectra of acetic acid and acetic acid-*d* isolated in CO₂ matrices have been investigated over the region 4000-450 cm⁻¹. Making use of the vibrational assignments previously reported for sodium acetate,⁶ a vibrational assignment of most of the fundamentals has been made for the two acids. The spectrum of acetic acid-*d* isolated in CO₂ matrix is shown in Figure 5.2. This approximate assignment of the bands observed for acetic acid isolated in a CO₂ matrix is given in Table 5.3. It is difficult or impossible to assign any features to $\nu(\text{O-H})$ or $\nu(\text{C-H})$ vibrations because they are obscured by intense absorptions of ice or CO₂. The C-C stretching vibration is associated with the band at 906 cm⁻¹ (858 cm⁻¹ in acetic acid-*d*) the frequency being lower than that in the acetate ion in agreement with the expected decrease of the contributor type to the resonance hybrid.

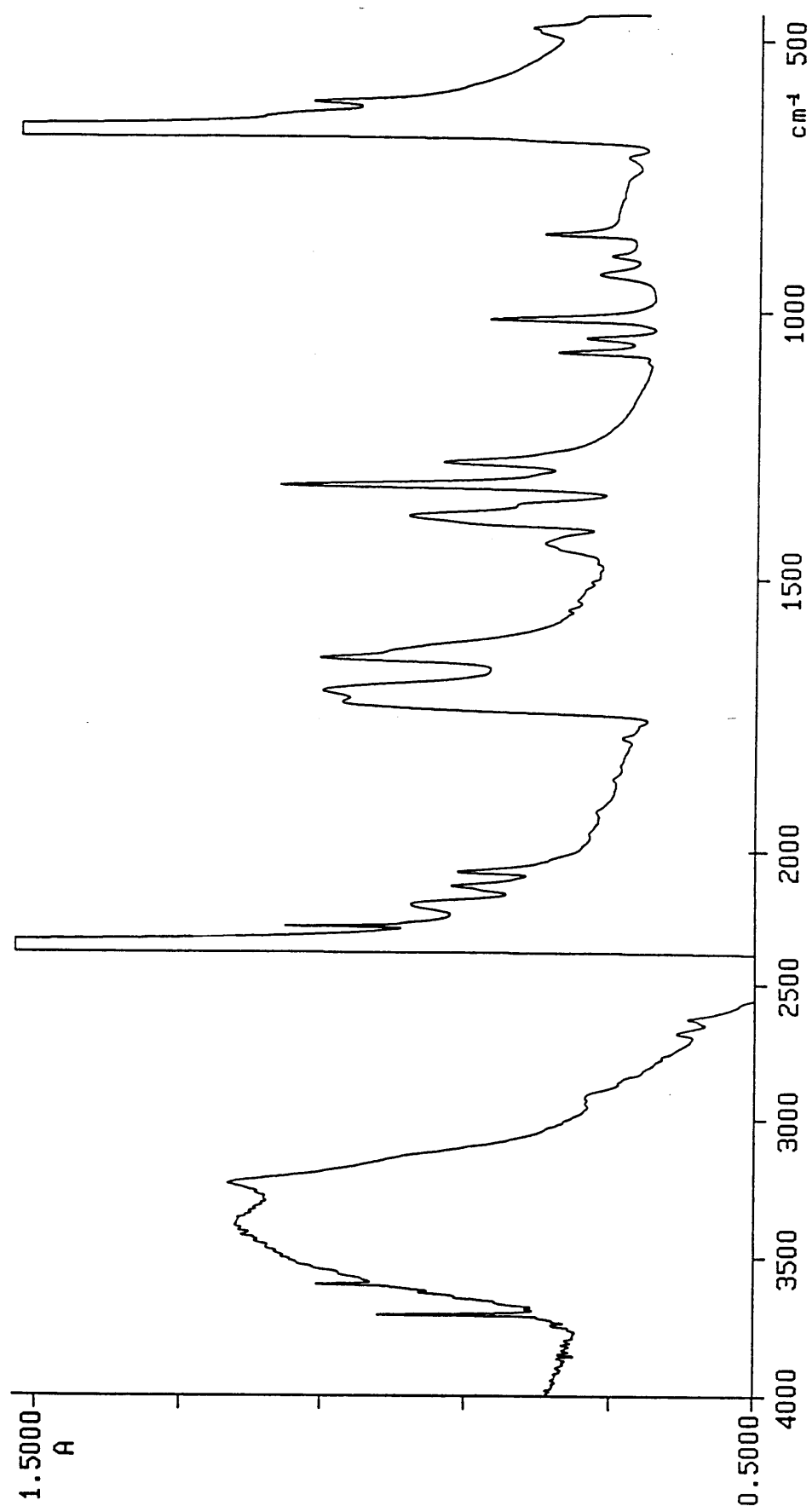


Figure 5.2 IR spectrum of acetic acid-*d*4 isolated in CO₂ matrix.

The band at 1715 cm⁻¹ in acetic acid, becomes 1705.5 cm⁻¹ in acetic acid-*d* and can be safely assigned to the C=O stretching vibration. By analogy with formic acid,⁷ the band at 638 cm⁻¹ is assigned to the OCO bending mode, while by analogy with sodium acetate,⁶ the band at 490 cm⁻¹ is assigned to the rocking vibration of the carboxyl group.

Table 5.3 Fundamental frequencies^a of acetic acid, acetic acid-*d* and acetic-*d*₃ acid-*d*.

Assignment	CH ₃ COOH		CH ₃ COOD		CD ₃ COOD		CH ₃ COO ^{-c}
	CO ₂ MI ^b	Gas ^c	CO ₂ MI ^b	Gas ^c	CO ₂ MI ^b	Gas ^d	
CO ₂ rock.	490	536	474.5	536	592		-
OCO bend	638	654	612	654	609	645	-
C-C str.	906	846	858	837	806 837	925	923
CH ₃ rock	923.5 953	990	897.5 931	995	923.5	785 812	1014
COH bend	1022 1050	1192	1012 1048 1074	959	1016 1034 1046.5 1094	1000	-
C-O str.	1287 1303	1279	1281 1324	1272	1284	1280	-
CH ₃ sym. Bend	1362.5	1340	1360 1382	1323	1328 1357	1060	1341
CH ₃ unsym. Bend	1412 1424 1438	1401	1433	1387	1393.5 1427	1060	1407
C=O str.	1715	1799	1705.5 1727	1792	1712 1729.5	1760	-
CH ₃ sym. Str.	e	2961	e	2929	<i>f</i>	2111R	2941
CH ₃ unsym. Str.	e	2997	e	2957	<i>f</i>	2237R	3006
O-H str.	e	3577	e	2640	e	2660	-

^a All frequencies in cm⁻¹

^b This work

^c See reference 7

^d See reference 8

^e Bands obscured by intense ice absorptions

^f Bands obscured by intense CO₂ absorptions.

Of the remaining fundamentals, that at 1287 cm^{-1} , becoming 1281 cm^{-1} in acetic acid-*d*, is assigned to the C-O stretching mode, while that at 1022 cm^{-1} , becoming 1012 cm^{-1} in acetic acid-*d*, is assigned to the in-plane COH bending vibration. The two A'' torsional modes, corresponding to torsion about the C-C and C-O bonds, would both be expected to have very low frequencies ($<400\text{ cm}^{-1}$) and were not observed.

5.3.3 Acetic-*d*₃ Acid-*d*

The infrared spectrum of CD₃COOD in a CO₂ matrix (Figure 5.3) has been investigated in this work. An approximate assignment of most of the fundamental frequencies is given in Table 5.3 along with the frequencies of other isotopes of acetic acid for comparison. The infrared spectrum of CD₃COOD in the gaseous phase has been obtained by several investigators. The fundamental frequencies obtained by Weltner⁸ are listed in Table 5.3 for comparison.

According to Nakamoto and Kishada,⁹ who used the values of Wilmshurst⁷ and Weltner⁸ in their study, the ν_3 bands at 1280 cm^{-1} in CD₃COOD and that at 1272 cm^{-1} in CH₃COOD should be described as the coupling between C-O stretching and CD₃ (or CH₃)-C stretching modes, whereas the ν_3 band at 1279 cm^{-1} in CH₃COOH may be better described as the coupling between C-O stretching, CH₃-C stretching and C-O-H bending modes. This band was observed in the CO₂ matrix-isolated CD₃COOD spectrum at 1284 cm^{-1} and was assigned to the C-O stretching mode according to Weltner.⁸

On the contrary, Nakamoto *et al.*⁹ has assigned the ν_4 band at 1000 cm^{-1} in CD₃COOD and that at 959 cm^{-1} in CH₃COOD as the pure C-O-D bending mode, and that at 1192 cm^{-1} in CH₃COOH as the pure C-O-H bending mode. These were observed

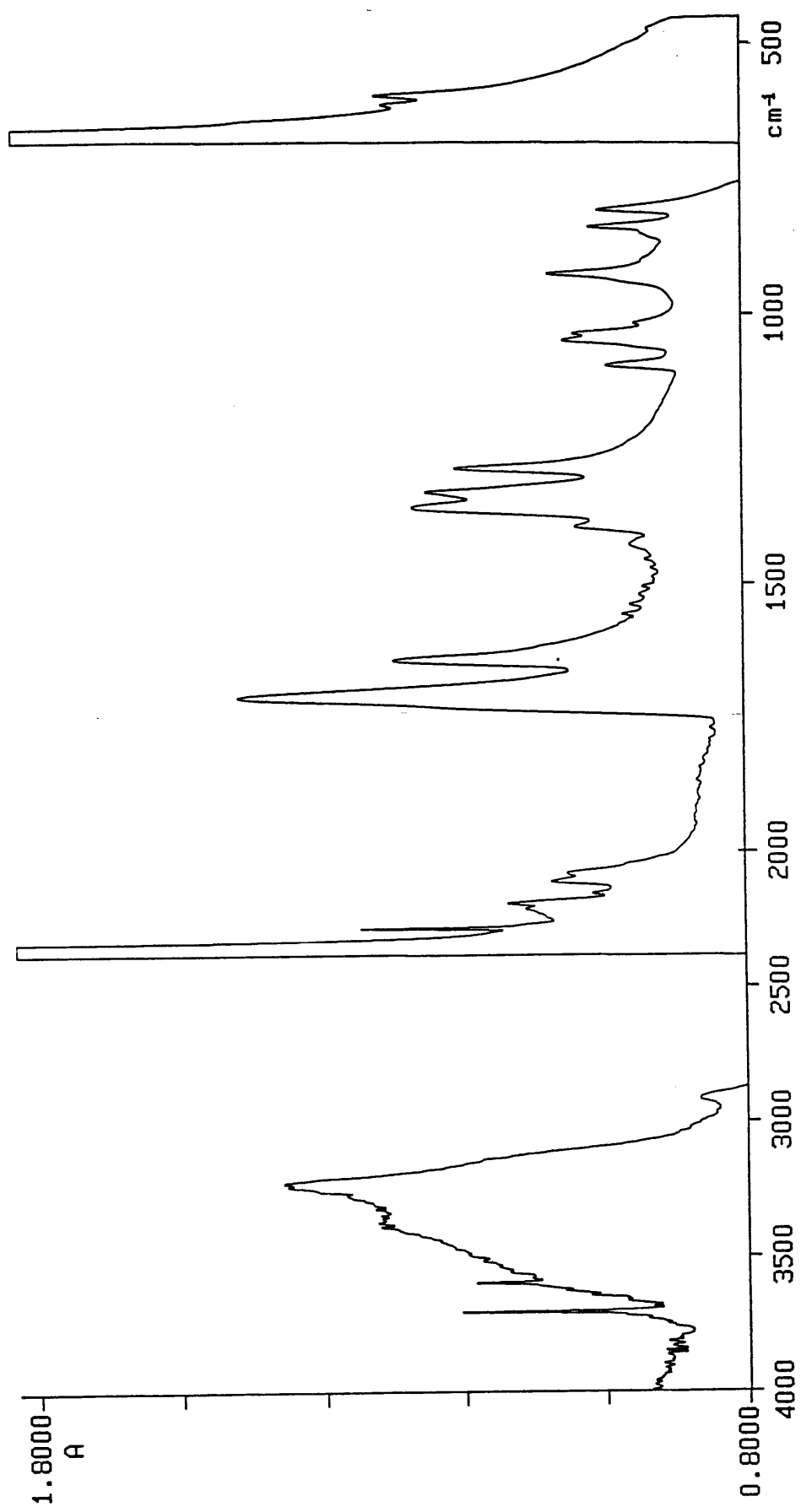


Figure 5.3 IR spectrum of acetic- d_3 acid- d isolated in CO_2 matrix.

in CO₂ matrix as multiple peaks. In CH₃COOH, this was observed as a well-resolved doublet at 1022 and 1050 cm⁻¹, while in CH₃COOD this was observed as a sharp peak at 1012 cm⁻¹ and a doublet at 1048 and 1074 cm⁻¹, and in CD₃COOD this was observed as a triplet at 1016, 1034 and 1046.5 cm⁻¹ and a fourth line at 1094 cm⁻¹. These assignments certainly explain the fact that ν_3 is little sensitive, whereas ν_4 is reasonably sensitive, to deuteration.

Another coupling was noticed by Nakamoto *et al.* is the ν_5 band of CD₃COOD (at 789 cm⁻¹) and that of CH₃COOD (at 837 cm⁻¹), which is a coupled vibration (see chapter 2) between the CD₃ (or CH₃)-C stretching and the C-O-D bending modes. These were observed in CO₂ matrix at 837 and 897.5 cm⁻¹ for CD₃COOD and CH₃COOD, respectively, and were assigned as C-C stretching mode according to Wilmshurst.⁷

Table 5. 4 Comparison between the frequencies of isotopic acetic acid in a CO₂ matrix and in the gas phase.

Assignment	CH ₃ COOD/ CH ₃ COOH ^a		CD ₃ COOD/ CH ₃ COOH ^a	
	CO ₂ MI	Gas	CO ₂ MI	Gas
CO ₂ rock.	0.968	1	1.208	0
OCO bend	0.959	1	0.955	0.986
C-C str.	0.947	0.989	0.907	1.093
CH ₃ rock	0.974	1.005	0.984	0.807
COH bend	1.008	0.804	1.011	0.839
C-O str.	1.006	0.995	0.992	1.001
CH ₃ sym. Bend	1.006	0.987	0.985	0.791
CH ₃ unsym. Bend	1.006	0.990	0.990	0.757
C=O str.	1.001	0.996	1.003	0.978
CH ₃ sym. Str.	b			
CH ₃ unsym. Str.	b			
O-H str.	b			

^a Ratios of CH₃COOD or CD₃COOD frequencies to CH₃COOH frequencies in CO₂ matrix and gas phase.

^b Bands obscured by intense absorptions of ice or CO₂.

To compare the frequency shifts occur on deuteration in the gaseous and CO₂ matrix isolated acetic acid the ratio of the frequency of the deuterated acid to that of the unlabelled acid is calculated and the results are shown in Table 5.4. In the case of double or multiple peaks, the average frequency is used in the calculation of the ratios. In the gas phase, CH₃COOD has the same frequencies as the CH₃COOH for all the absorptions and the ratios are close to 1 except for the COD bending and the O-D stretching vibrations which show considerable red shifts on deuteration and the ratios are 0.805 and 0.738, respectively. This is expected as these two bands are the only ones which are affected by the deuteration. Gaseous CD₃COOD shows red shifts in most of the frequencies as most of the molecular vibrations are affected by the deuteration. The absorptions assigned to CD₃ rocking, COD bending, CH₃ symmetrical bending, CD₃ unsymmetrical bending, CD₃ symmetrical stretching, CD₃ unsymmetrical stretching and OD stretching give ratios between 0.712 and 0.839 while the rest of the bands show almost the same frequencies as those of CH₃COOH.

As mentioned in Section 2.4 the frequency of a fundamental in the infrared spectrum is given approximately by:

$$\nu \propto (f/\mu)^{1/2}$$

where f is the force constant of the bond and μ is the reduced mass, given by $(m_1 m_2)/(m_1 + m_2)$. Upon isotopic substitution of, say atom m_1 by a heavier isotope m_1^* , e.g. of hydrogen by deuterium, reduced mass will necessarily change. However, the force constant is unchanged. Thus for two isotopic species where the reduced masses are μ_1 and μ_2 respectively we may calculate a frequency *ratio* from:

$$\frac{\nu_1}{\nu_2} = \left(\frac{\mu_1}{\mu_2} \right)^{1/2}$$

The situation is complicated for complex polyatomics partly due to vibrational coupling. Thus, for example, substitution of hydrogen by deuterium in the molecule ethanol would not be expected to affect the frequency of $\nu(\text{C-O})$ because no motion of an H atom is involved in this vibration. In fact a frequency shift is seen because the $\nu(\text{C-O})$ vibration is coupled to other vibrations where motion of H atoms does occur.

In the CO_2 matrix, on the other hand, CH_3COOD gives almost the same frequencies as CH_3COOH for all the bands including the COD bending mode. The O-H vibration in CH_3COOH and O-D vibration in CH_3COOD cannot be identified with any degree of certainty. Also all the bands of CD_3COOD give frequency ratios of ~ 1 when compared to CH_3COOH bands although it was expected to observe red shifts in the frequencies of some absorptions on deuteration as in the gaseous phase. The only band that shows a frequency shift is the CO_2 rocking band which gives a ratio of 1.208 even though it should not be affected by the deuteration. These results are somewhat worrying and are not easy to explain. Repeat experiments have failed to reveal bands of deuterated acetic acid isolated in a CO_2 matrix showing the expected frequency shifts. Conversion of CH_3COOD to CH_3COOH or of CD_3COOD to CD_3COOH by exchange with traces of moisture in the apparatus is quite possible. However, conversion of the CD_3 group of CD_3COOD to CH_3 is much harder to explain. One possibility is that traces of non-deuterated acetic acid are trapped in the apparatus and that this is deposited preferentially. However, the situation remains unclear and more experiments are required to understand this unexpected result.

5.3.4 Formic-*d* Acid-*d*

Previous workers¹⁰⁻¹² have made infrared studies of deuterated forms of monomeric formic acid from 4000 cm⁻¹ to 650 cm⁻¹ with a low dispersion instrument. They had hoped that vibrational modes associated with the OCO core of the molecule would maintain fairly constant frequencies of absorption with deuteration while those arising from a motion of the hydrogen atoms would shift by a predictable amount. If this had proved true it might have been possible to assign some of the observed frequencies to characteristic modes. As such behaviour was not observed in the low dispersion studies, the spectra from 3700 cm⁻¹ to 800 cm⁻¹ were studied by Williams¹³ under high resolution in the hope that the additional band structure would be of further aid in the assignment. The generally quoted fundamental frequencies of formic acid monomers are based on the work of Milliken and Pitzer¹⁴ and Miyazawa and Pitzer,¹⁵ who combined their vapour phase and nitrogen matrix data with the previous observations of Williams.¹³

The infrared spectrum of DCOOD in CO₂ matrix is shown in Figure 5.4. A complete assignment of the fundamental frequencies observed for HCOOH and DCOOD isolated in CO₂ matrix are listed in Table 5.5 along with the values of Redington¹⁶ for vapour phase and neon matrix-isolated DCOOD for comparison. In CO₂ matrix isolated HCOOH, the O-H stretching band occurs as a triplet at 2902, 2757 and 2586 cm⁻¹. The C-H and C=O stretching frequencies were assigned to the bands at 2958 and 1712 cm⁻¹. These three bands were observed in matrix-isolated DCOOD at 2606, a doublet at 2098 and 2035 and 1700 cm⁻¹, respectively. It should be noted (see Table 5.5) that some of these assignments are necessarily tentative because of overlap with strong absorption bands of ice or CO₂. It has already been mentioned that in

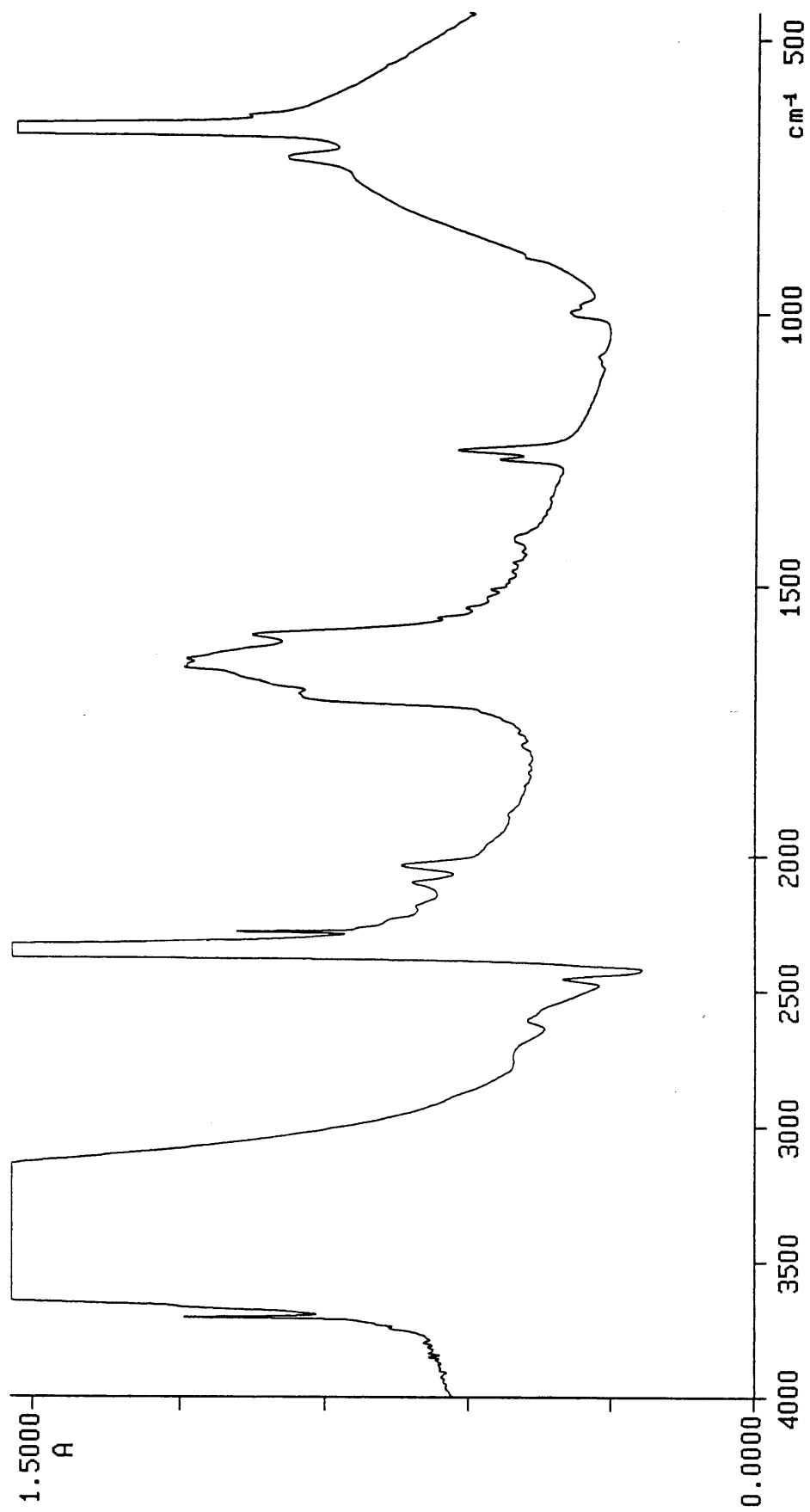


Figure 5.4 IR spectrum of formic-*d* acid-*d* isolated in CO₂ matrix.

HCOOH ν_{C-C} and δ_{COH} are considered to be interacting slightly, increasing the former and lowering the latter from their expected unperturbed frequencies by a few wavenumbers.⁷ The C-H bending mode is associated with the doublet at 1392 and 1377 cm^{-1} in HCOOH by analogy with Fonteyne's assignment¹⁷ of a band at 1386 cm^{-1} in the formate ion to this mode and the assignment of Miller *et. al.*¹⁸ to the band at 1381 cm^{-1} also to the C-H bending. On deuteration of formic acid to give formic-*d* acid-*d*, ν_{C-O} would be expected to remain constant or decrease very slightly.⁷ The ν_{C-O} occurs at its expected position, again as doublet at 1261 and 1225 cm^{-1} , while δ_{C-D} has dropped to 1040 cm^{-1} and δ_{COD} decreased to 945 cm^{-1} .

Table 5.5 Fundamental frequencies^a of HCOOH and DCOOD

HCOOH		DCOOD			Assignment ^b
Gas ^b	Ne matrix ^b	Gas ^b	Ne matrix ^b	CO ₂ matrix ^c	
3570.0	3569.4	2632	2632.1	2606	OD str.
2943.8	2937.8	2232	2200.0	2098 ^d	CD str.
				2035	
1776.2	1773.9	1742	1725.5	1700 ^e	C=O str.
1387.0	1379.7	1171	1170.5	1261	C-O str.
				1225	
1223.0	1217.6	1040	1031.9	1040	DCO-COD def.
1105.4	1102.8	945	944.9	945	COD-DCO def.
625.4	625.9	558	554.9		OCO-COD def.
1033.4	1035.6	873	874.8		CD wag.
641.8	637.6	491	490.4		COD tor.

^a All frequencies in cm^{-1}

^b See reference 16

^c This work

^d Tentative assignment – band partially obscured by intense CO₂ absorption

^e Tentative assignment – band partially obscured by intense ice absorption

The frequency shifts which occur on deuteration in the gaseous and CO₂ matrix isolated formic acid were compared by calculating the ratios of the frequencies of the deuterated acid to those of the unlabelled acid and the results are shown in Table 5.6. A similar procedure had previously been adopted for deuterated and non-deuterated acetic acid (see Table 5.4). In the gas phase, considerable red shifts are observed in the

frequencies of the $\nu(\text{OD})$, $\nu(\text{CD})$ and the COD torsion vibrations as the DCOOD/HCOOH ratios are around 0.75 as these modes are most affected by the deuteration. The rest of the frequencies show lower shifts as the ratios are around 0.85. The C=O stretching frequency shows a ratio close to 1. In CO_2 matrix the modes which are affected more by the deuteration are the $\nu(\text{OD})$ and the $\nu(\text{CD})$ vibrations and the ratios are 0.72 and 0.71, respectively. The rest of the vibrations gave ratios close to 1 as they are not affected by the deuteration. These results are entirely as expected showing relatively small changes between the isotopic shifts observed for the gas phase and matrix isolated molecules. These subtle changes probably reflect somewhat different couplings between the vibrational modes in the two environments.

Table 5. 6 Comparison between the frequencies of isotopic formic acid in a CO_2 matrix and in the gas phase.

<u>Assignment</u>	<u>DCOOD/HCOOH^a</u>	
	<u>CO_2 MI</u>	<u>Gas</u>
OD str.	0.724	0.737
CD str.	0.709	0.758
C=O str.	0.993	0.981
C-O str.	1	0.844
DCO-COD def.	1.026	0.850
COD-DCO def.	0.991	0.855

^a Ratios of HCOOD frequencies to HCOOH frequencies in CO_2 matrix and gas phase.

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6.1 Introduction

Because hydrocarbon levels in the ambient air are typically below the detection limit of most of the detectors, cryogenic or sorbent concentration techniques are necessary to increase sensitivity. Cryogenic concentration has been shown to be effective in the trapping of these volatile species.¹ The determination of volatile organic compounds (VOCs) in the air of the non-industrial environment requires an enrichment step in most techniques; methods commonly used are absorption in solvents, cryotrapping or adsorption on solid sorbents.² Desorption of compounds enriched on solid sorbents may be performed with liquids or thermally.

Activated charcoal is used as an adsorbent. Due to its high surface activity, chemical reaction may occur during storage of the samples. Often very low recoveries are found in the ppb range because of partial decomposition of the sampled compounds and strong adsorptive behaviour.³

On the other hand, polymeric adsorption materials are less reactive or even inert, but have lower retention volumes for VOC.⁴ The resulting loss of sensitivity, compared to activated charcoal, can be overcome by thermal desorption, where the sample is directly transferred to the separation column. For qualitative or quantitative determinations, the measurement system must be well characterized. This implies some knowledge about adsorption and desorption behaviour of the adsorbents used.

Tenax is a widespread adsorbent used in the field of air analysis.^{5,6} It is claimed to be inert with respect to sampled compounds.⁷ No chemical reaction were observed in

the presence of substantial amounts of ozone.⁸ On the other hand, Zielinska *et al*⁹ found some nitroderivative artifacts when desorbing PAH in the presence of nitric oxides.

Tenax TA is a further development of Tenax GC. It can be cleaned simply by heating in an inert gas flow,^{4,10} is stable up to 280°C and produces less artifacts than Tenax GC.¹¹ Carbotrap is a very pure graphitised carbon black. It can easily be cleaned thermally in an inert gas flow.¹⁰ Carbotrap is said to be free of contaminants and not susceptible to sorbent degradation.¹² Nevertheless, tiny impurities in the adsorbent could act as specific active sites.¹³

The two most useful adsorbents are silica gel and activated carbon, which differ in several respects. Silica gel is polar and will consequently show pronounced selectivity in preferentially adsorbing polar molecules, in particular water. Hence, when sampling large volumes, the atmospheric moisture may compete for the adsorption sites and displace the compound being sought, especially if this is nonpolar. Thus, it can be shown that the silica gel absorption tube described above may become saturated with water when the sample volume is only 3 litres, and the retentive properties of the silica gel may be impaired as sample volumes of this size are approached. Desorption from silica gel is relatively easier than for carbon, but will be more difficult for the more strongly held polar compounds.¹⁴

Activated carbon is nonpolar and will consequently generally adsorb organic vapours in preference to water, so that atmospheric moisture will not interfere with the sampling of large volumes; however, desorption is generally more difficult than from silica gel.

Although the adsorptive capacities of both silica gel and activated carbon will be much greater in general than the amount of analyte to be adsorbed, in practice it will be their retentivities, i.e., the maximum amount of the compound retained when exposed to

uncontaminated air, that will decide their suitability, since the concentration of analyte in the sample volume will always be low.

6.2 Sample Collection Using Adsorbents

The LpDNPH (low pressure drop dinitrophenylhydrazine) S10 cartridge is an air sampling device designed for sampling carbonyls in ambient, indoor, and industrial atmosphere. Carbonyls are trapped on a high purity silica adsorbent coated with 2,4-dinitrophenylhydrazine, where they are converted to the hydrazone derivatives. The cartridge is connected to the vacuum line using appropriate adapters. The air sample is collected in the direction of the arrow. After sampling, both ends of the cartridge are capped immediately. The cartridge is stored at 4°C and protected from light. The sample is analyzed within 30 days of sampling. Mixtures of known amounts of acetone and acetaldehyde vapours are prepared and introduced to the cartridge instead of the air sample to test the cartridge efficiency. The mixture bulb is connected to the cartridge which is connected to the main line from the other end as shown in Figure 6.1.

Sample desorption is done either thermally or by eluting the cartridge with acetonitrile using gravity feed. The cartridge is eluted with 2 mL aliquots of acetonitrile and the eluate is collected to the 5.0 mL mark on a volumetric flask. Ideally, desorption is in the direction opposite that of the air flow during sample collection. The extract is stored at 4°C until analysis. In another set of experiments, acetonitrile vapour has been passed through the cartridge instead of liquid acetonitrile to avoid any loss of the carbonyl compounds in the liquid since they are present in very low concentrations. In this case the air sample or the known mixture is passed through the cartridge which is

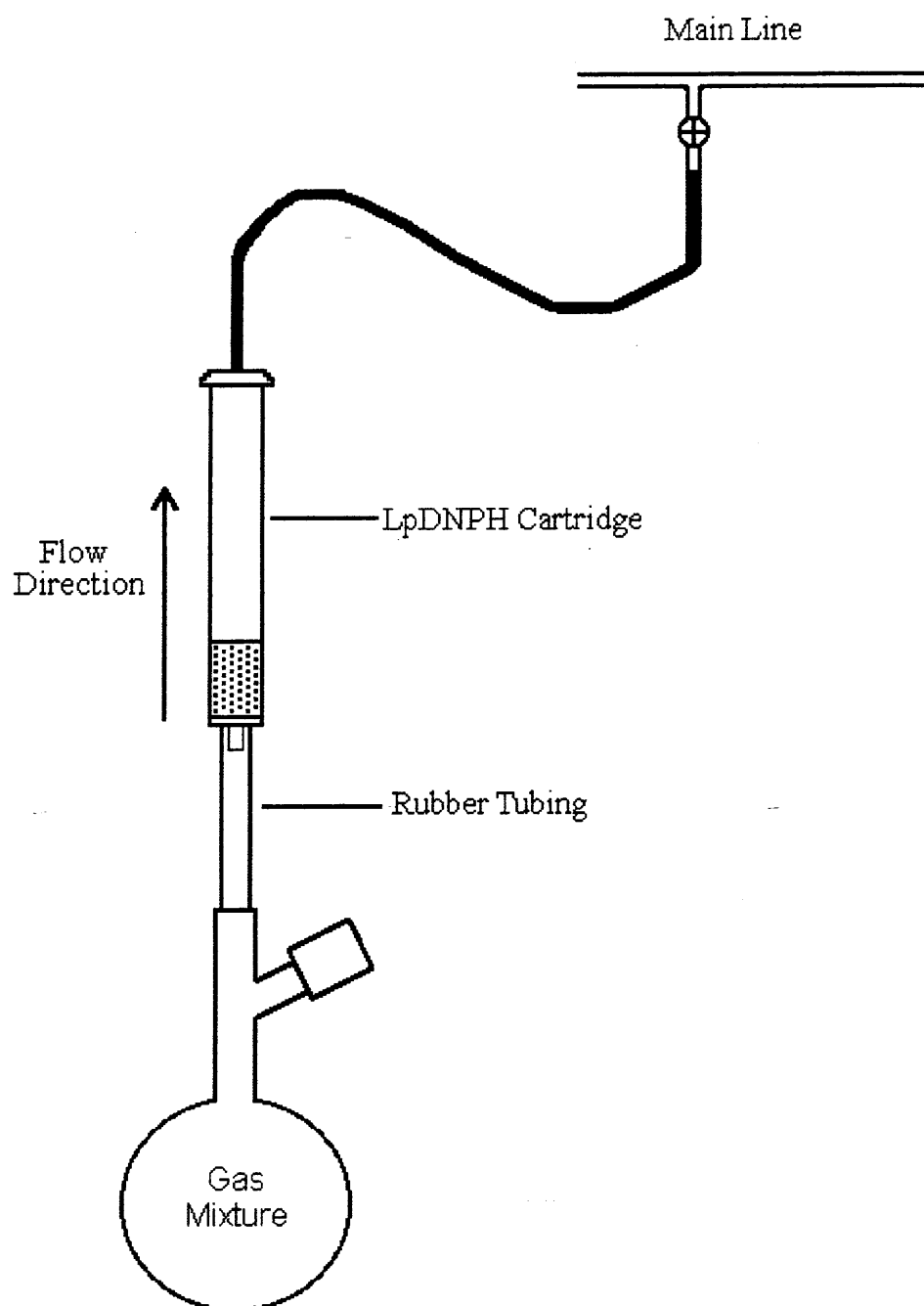


Figure 6.1 Adsorption of gas mixture into an LpDNPH cartridge.

connected to the main vacuum line. An evacuated bulb is filled with about 60 Torr acetonitrile vapour and connected to one end of the cartridge which is connected to the cold cell from the other end as shown in Figure 6.2 so that the acetonitrile flow is in the opposite direction of the air flow during sampling. Rubber tubing is used for all the connections. The cold cell reservoir is filled with liquid nitrogen to cool the window to 77 K then the acetonitrile bulb is opened to pass the acetonitrile through the cartridge and desorb all the sample from the adsorbent material and at the same time deposit the acetonitrile-sample mixture onto the cold window very slowly to get a solid film and IR spectrum is obtained for that sample. For the analysis of the spectra obtained using the LpDNPH cartridge, IR spectrum of solid acetonitrile (Figure 6.3) is obtained at 77 K and subtracted from the sample spectra.

The analysis of car exhaust using the LpDNPH cartridge was studied. The cartridge was connected to an evacuated 6L bulb using rubber tubing and car exhaust was collected from the other end of the cartridge by opening the bulb valve very slowly to allow the car exhaust to be drawn through the cartridge. The adsorbed sample was desorbed by elution with acetonitrile vapour while depositing onto the cold cell. The IR spectrum of the sample is shown in Figure 6.4. The lines shown in the spectrum are very sharp and well-resolved. Most of the absorptions are due to acetonitrile since they have not been subtracted from the spectrum. The new absorptions which are assigned to the sample are those at 534, 1095, 1228 and 1708 cm^{-1} . By comparing the frequencies of these absorptions with those observed earlier for the carbonyl compounds, all of these absorptions can be assigned to acetone (see Table 4.1). The broad peak at 3263 cm^{-1} which appears in a very high intensity can be assigned to water vapour. From these observations it is thought that the LpDNPH cartridge is suitable for use in the analysis

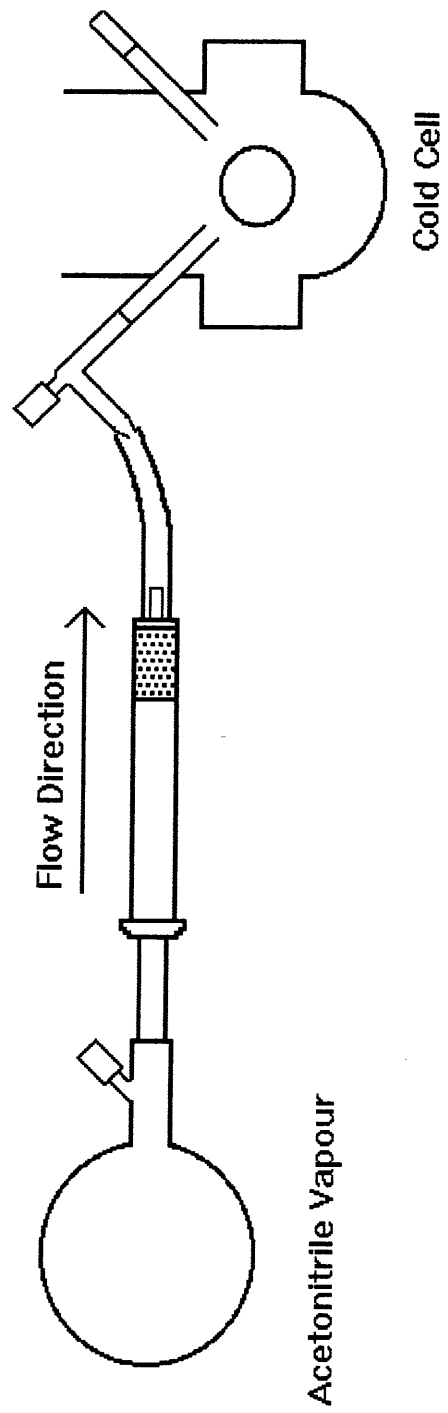


Figure 6.2 Sample desorption by elution with acetonitrile vapour.

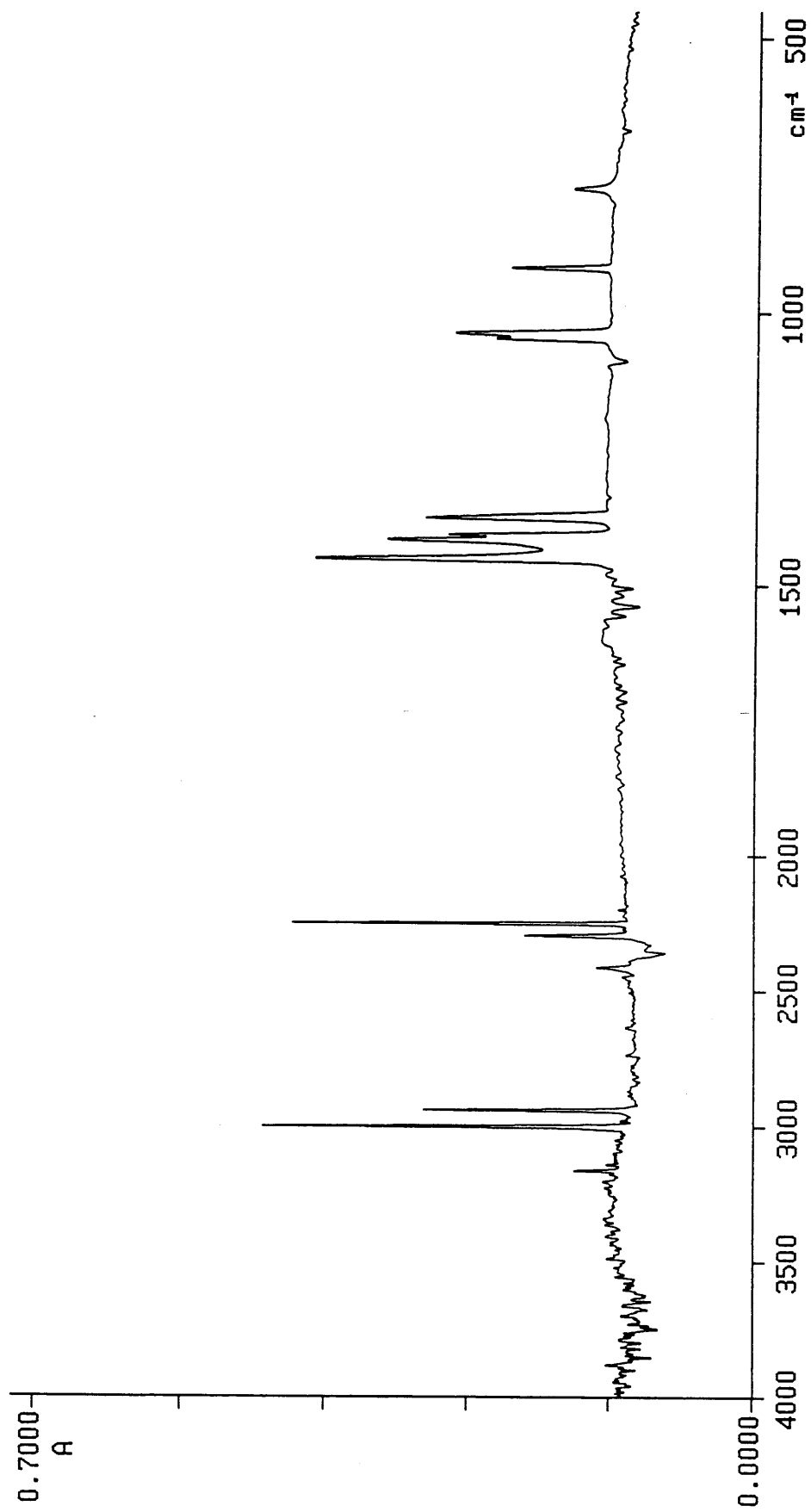


Figure 6.3 IR spectrum of solid acetonitrile.

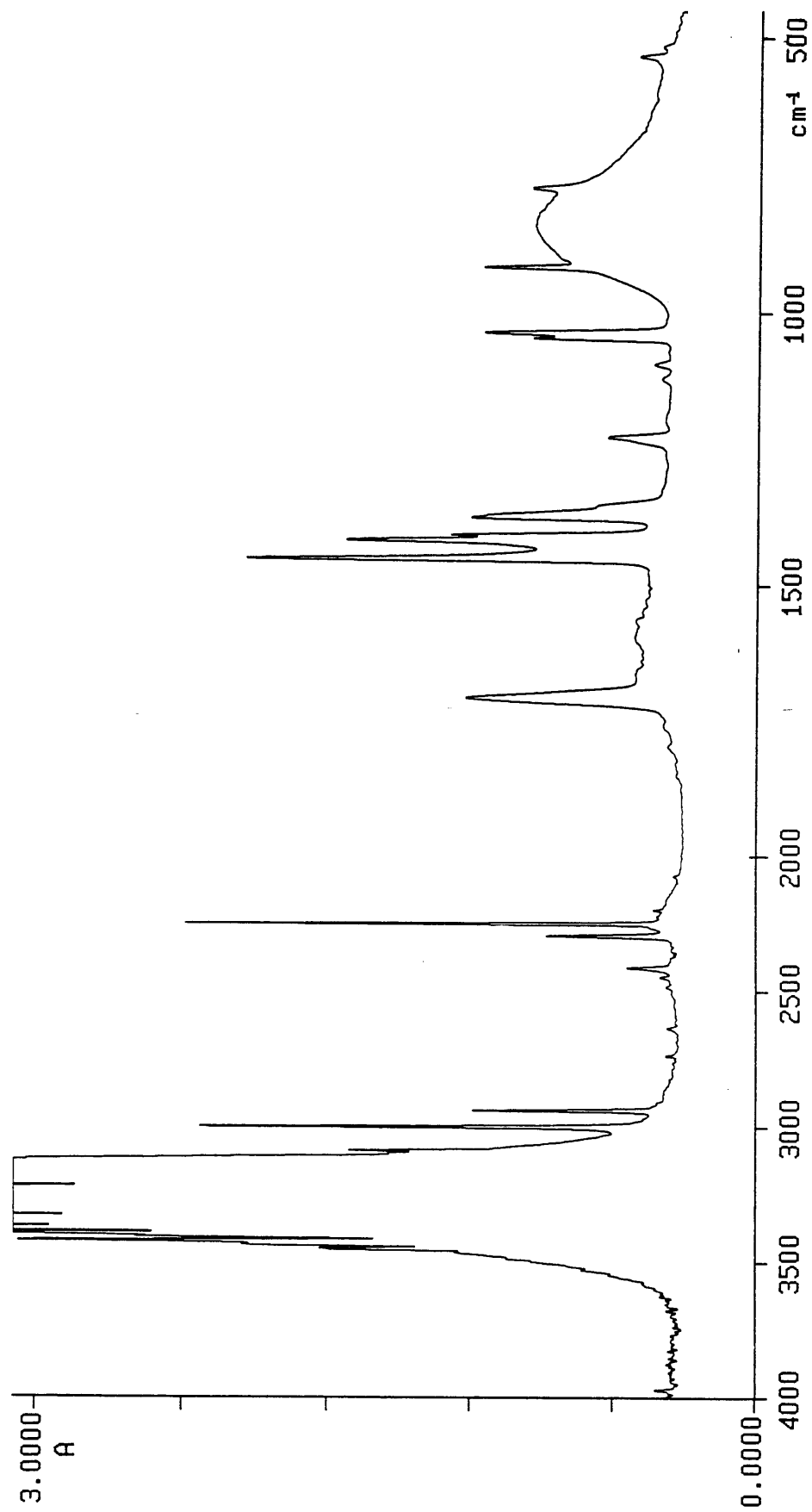


Figure 6.4 IR spectrum of car exhaust sample adsorbed onto an LpDNPH cartridge and desorbed with acetonitrile vapour.

of carbonyl compounds, e.g. in car exhaust or in the atmosphere. Analysis of mixtures of known compounds at known concentrations should be carried out, however, if quantitative analysis is to be performed. The problem in using this cartridge is that CO_2 is not adsorbed onto the cartridge adsorbent material. Therefore, in order to trap the desorbed material in a CO_2 matrix, CO_2 would have to be added externally to the desorbed material. This would make quantitative analysis much more difficult. As such a range of other adsorbents were studied (see Section 6.4). In the experiment on car exhaust described here acetone is deposited as a solid film along with acetonitrile and a small amount of water. The spectrum of this deposit clearly gives useful qualitative but not quantitative data.

6.3 Thermal Desorption

Thermal desorption is done using a warming tape. Using the portable line, the mixture bulb is connected to the cartridge which is connected to position 7 on the line. All taps are opened to adsorb the mixture into the cartridge. This step is done very slowly for a better adsorption and after about 5 minutes the bulb tap is closed. A Dewar full of liquid nitrogen is placed around the coil and after the coil becomes cold the cartridge is wrapped with a warming tape and the temperature is controlled to reach about 80°C so that any desorbed compound is trapped into the cold coil at 77 K. After about 30 minutes the warming tape and the cartridge are removed and tap 5 is closed. The cold cell which is connected to the main line is prepared for sample deposition. A rubber tube is connected between the deposition point on the cold cell and position 7 on the portable line. The liquid nitrogen Dewar is removed and the coil is warmed to melt

all the frozen compounds and at the same time to deposit them onto the cold window.

The IR spectrum is recorded for this sample.

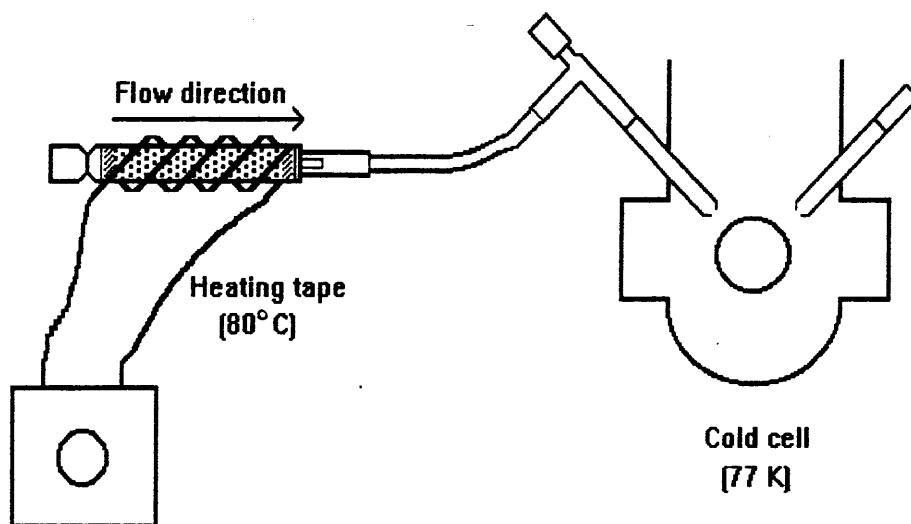


Figure 6.5 Thermal desorption of pollutants from the adsorbent tube while depositing onto the cold window at 77 K.

A simpler method was followed so that thermal desorption and sample deposition are done simultaneously by connecting the adsorbent cartridge to the deposition point on the cold cell and wrapping it with the warming tape (Figure 6.5). The cell reservoir is filled with liquid nitrogen and after the window reached 77 K the temperature controller is switched on and set to 80°C. The solid film of the desorbed compounds is formed and after about 30 minutes the warming tape and the cartridge are removed and the IR spectrum is recorded.

6.4 Other Adsorbents

The selection of an adsorbent material for an application is based on a large number of variables. These variables originate from three sources and each must be evaluated before a material is selected.

Purge and trap sampling system

Before an adsorbent material is selected the sample matrix, the range of analytes required for analysis and the concentration of analytes in the sample must all be considered. In conjunction with this the limits of detection and the amount of sample available for analysis must also be considered. All of these factors are interrelated. Based on the limits of detection and the concentration of analytes in the sample the minimum sample size required for analysis can be determined. Depending on the range of analytes required for analysis the sample collection temperature can be determined. The higher the temperature of the sample the higher the boiling point range of analytes that will be collected. Depending on the temperature of the sample and the amount of water in the sample the sample purge flow rate and need for a dry purge make-up gas can be determined.

Adsorbent resin – Sample collection conditions

Next based on the data above plus the range of analytes required for the analysis, an adsorbent resin must be selected. The Breakthrough Volume Data tables¹⁵ can be used to help select a resin. For the collection of samples with the desorption tube

at room temperature the Breakthrough Volumes for all the analytes of interest should be greater than 10.0 litres per gram of adsorbent resin. This value can be lowered only if gas volumes less than 5.0 litres per gram of adsorbent resin are used during sample collection. Next the adsorbent resin must be evaluated for its affinity for water. Also the dimensions of the desorption tube including the amount of adsorbent resin that it can hold must be considered. Related to this, the backpressure generated inside the desorption tube must be considered if a small sampling pump is used for sample collection.

Adsorbent resin – Desorption system conditions

Finally the desorption parameters must be considered. Again the Breakthrough Volume tables are used to determine the temperature required to release the analytes of interest off the adsorbent resin. This temperature must be less than the maximum rated temperature of the adsorbent resin. Related to this is the gas volume required to release the analytes off the adsorbent resin. A desorption temperature must be selected that will release the analytes of interest off the adsorbent resin in less than 10 mL/g of adsorbent resin.

A comparison between the efficiency of different materials in adsorbing carbonyl compounds was done. Glass tubes with one tipped end were packed with different materials such as activated carbon, alumina, kieselguhr or molecular sieve (aluminium calcium silicate). The materials were activated by heating them in oven at 120°C overnight to get rid of any adsorbed water. As shown in Figure 6.6, the glass tubes were packed with about 5 cm high of the adsorbent material and plugged with a

piece of filter paper and glass wool at both ends. All the adsorption and the thermal desorption procedures were done using these adsorbing tubes. The tubes were repacked for each new sample.

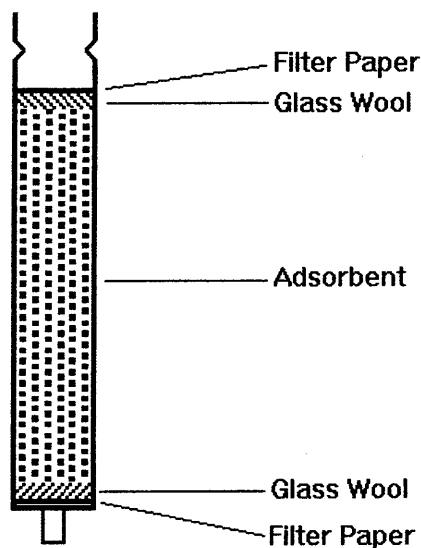


Figure 6.6 The adsorbent tube prepared for pre-concentration of pollutants

Each of the carbonyl compounds (acetone, acetaldehyde, acetic acid or formic acid) was adsorbed in the four different columns (carbon, alumina, kieselguhr or molecular sieve), as shown in Figure 6.7, in order to study the adsorbence efficiency for each column (quantitative analysis). First, a mixture of 2.5% of acetone in CO_2 was prepared in an external bulb then diluted with CO_2 to get a concentration of 0.2% acetone in CO_2 . The diluted mixture was adsorbed onto a carbon column then thermally desorbed and deposited onto the cold cell and the IR spectrum was recorded. The compound to CO_2 peak area ratio was calculated and compared with that obtained from

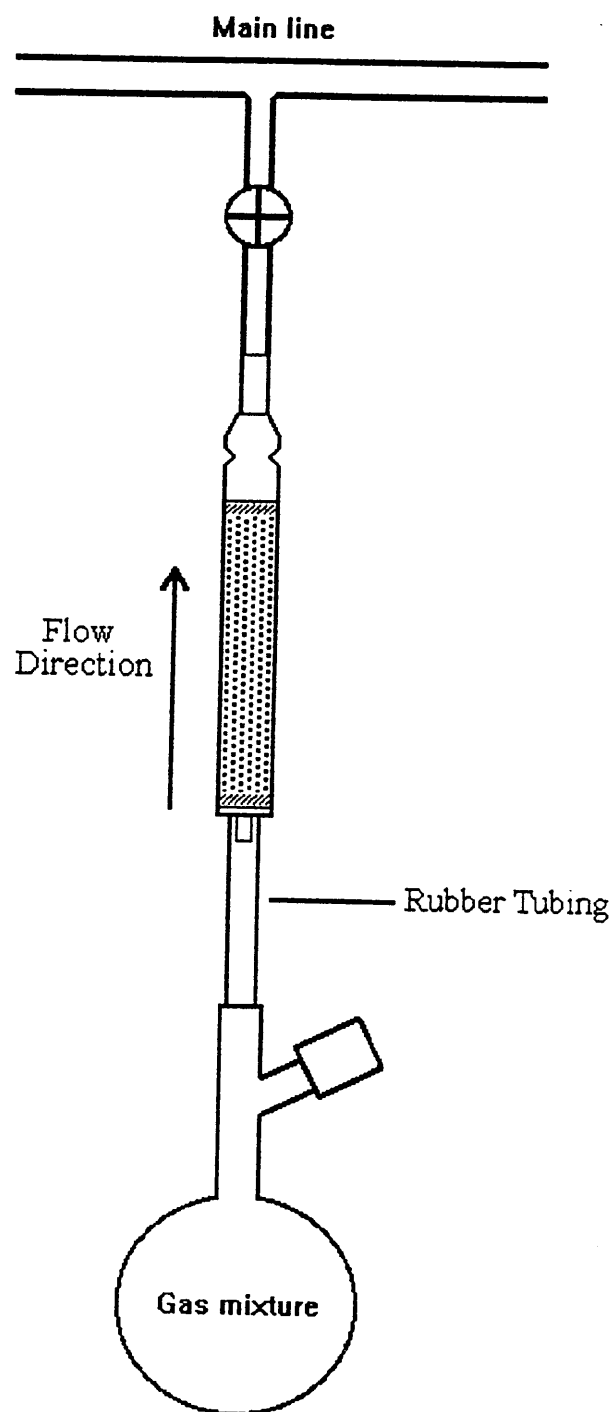


Figure 6.7 Adsorption of gas mixture into an adsorption tube

the calibration curve of acetone (Figure 4.19). The procedure was repeated with mixtures of the same concentration of acetone in CO₂ using the other adsorbent columns. The procedure then was repeated for acetaldehyde (0.2%), acetic acid (0.5%) and formic acid (0.5%) using the four types of adsorbent columns. The percentage recovery of the compounds using these adsorbents was calculated by comparing the peak area ratios obtained after the desorption to those obtained from the calibration curves constructed in the early stage of this study. The procedure was repeated 3 times to study the reproducibility. The result is shown in Table 6.1. Each adsorbent gives different percentage of recovery and the best was the activated carbon which gave a percentage recovery between 85 and 90%. The carbon adsorbent tube, therefore, has been used in the rest of this work for either laboratory experiments or field work. The tubes were packed with 1.6-1.8 g of activated carbon.

As an example, two mixtures of the same concentration (0.2%) of acetone in CO₂ were adsorbed onto two carbon adsorbent tubes. To test the trapping efficiencies of acetone on the carbon adsorbent tube, one sample has been thermally desorbed after one hour and the other after 24 hours. The percentage recoveries have been calculated by comparing the peak area ratios obtained after the desorption to those obtained from the standard calibration curves. This was repeated 3 times to study the reproducibility. Recoveries are $86.6 \pm 1.8\%$ at 1 hour and $85.5 \pm 1.3\%$ at 24 hours. The same procedure was repeated for mixtures of 0.5% acetic acid in CO₂. Recoveries are $86.8 \pm 3.3\%$ at 1 hour and $86.1 \pm 2.8\%$ at 24 hours. Recoveries did not decrease much with time, indicating that the carbonyl compounds, once trapped on the carbon adsorbent tubes, can remain there during the sample collection or during storage before the analysis.

Table 6.1 Percentage recovery using different adsorbents

	<u>Carbon</u>	<u>Alumina</u>	<u>Kieselguhr</u>	<u>Molecular sieve</u>
0.2% Acetone	87.6 $\pm$ 2.8	80.2 $\pm$ 2.8	69.8 $\pm$ 6.0	74.1 $\pm$ 4.9
0.2% Acetaldehyde	89.2 $\pm$ 1.6	80.6 $\pm$ 1.6	72.2 $\pm$ 3.2	77.4 $\pm$ 3.9
0.5% Acetic acid	88.0 $\pm$ 0.7	82.4 $\pm$ 1.2	68.2 $\pm$ 3.7	74.6 $\pm$ 4.1
0.5% Formic acid	89.0 $\pm$ 1.8	77.9 $\pm$ 2.6	67.0 $\pm$ 2.0	75.4 $\pm$ 2.6

For qualitative analysis, 7 mixtures of acetone and acetaldehyde in CO₂ were prepared in different ratios keeping the total concentration of the compounds in CO₂ constant (about 20%). The mixtures were passed through carbon tubes then thermally desorbed while depositing onto the cold window and IR spectra were recorded (Figure 6.8). Two absorptions were distinguished in the $\nu(\text{C}=\text{O})$ region. They were assigned to the $\nu(\text{C}=\text{O})$ absorption of acetone at about 1710 cm⁻¹ and the $\nu(\text{C}=\text{O})$ absorption of acetaldehyde at about 1720 cm⁻¹. The peak heights of the two bands were measured (Table 6.2) and the peak height ratio of acetone to acetaldehyde (Ratio X) was calculated for each spectrum and plotted against the acetone mole fraction (Figure 6.9).

The same experiment was repeated with 7 mixtures of formic acid and acetic acid in CO₂. The total concentration was kept around 12% in all mixtures. An IR spectrum was recorded for each mixture after being passed through carbon tube, thermally desorbed then deposited onto the cold window. A typical spectrum of a formic acid/acetic acid mixture is shown in Figure 6.10. Again two absorptions are distinguished in the $\nu(\text{C}=\text{O})$ region. They are assigned to the $\nu(\text{C}=\text{O})$ absorption of formic acid at about 1722 cm⁻¹ and the $\nu(\text{C}=\text{O})$ absorption of acetic acid at about 1711

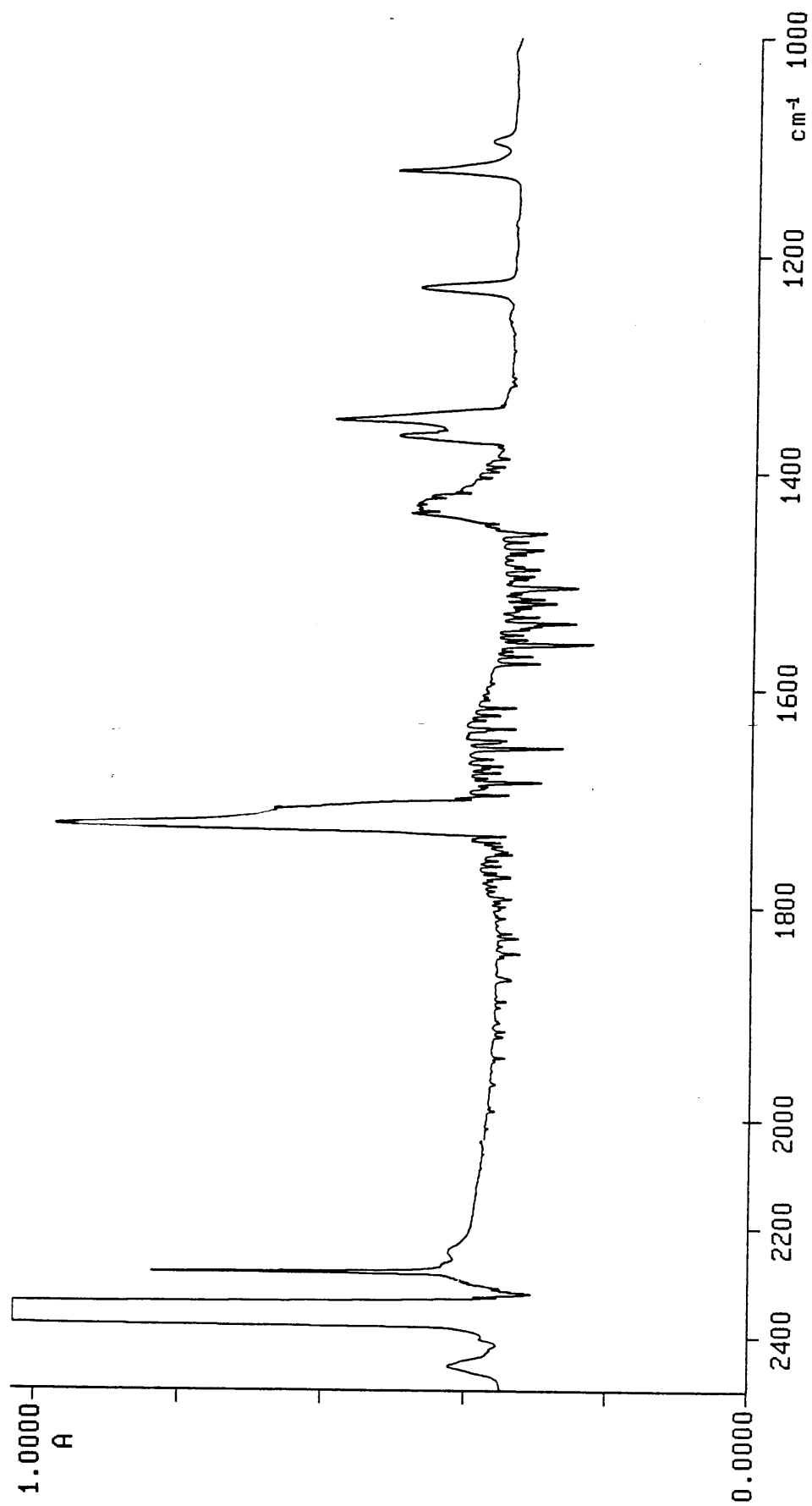


Figure 6.8 (a) IR spectrum of 2:4 mixture of acetone and acetaldehyde in CO₂ matrix after being adsorbed onto a carbon adsorbent tube.
Note lines of water vapour due to poor background subtraction.

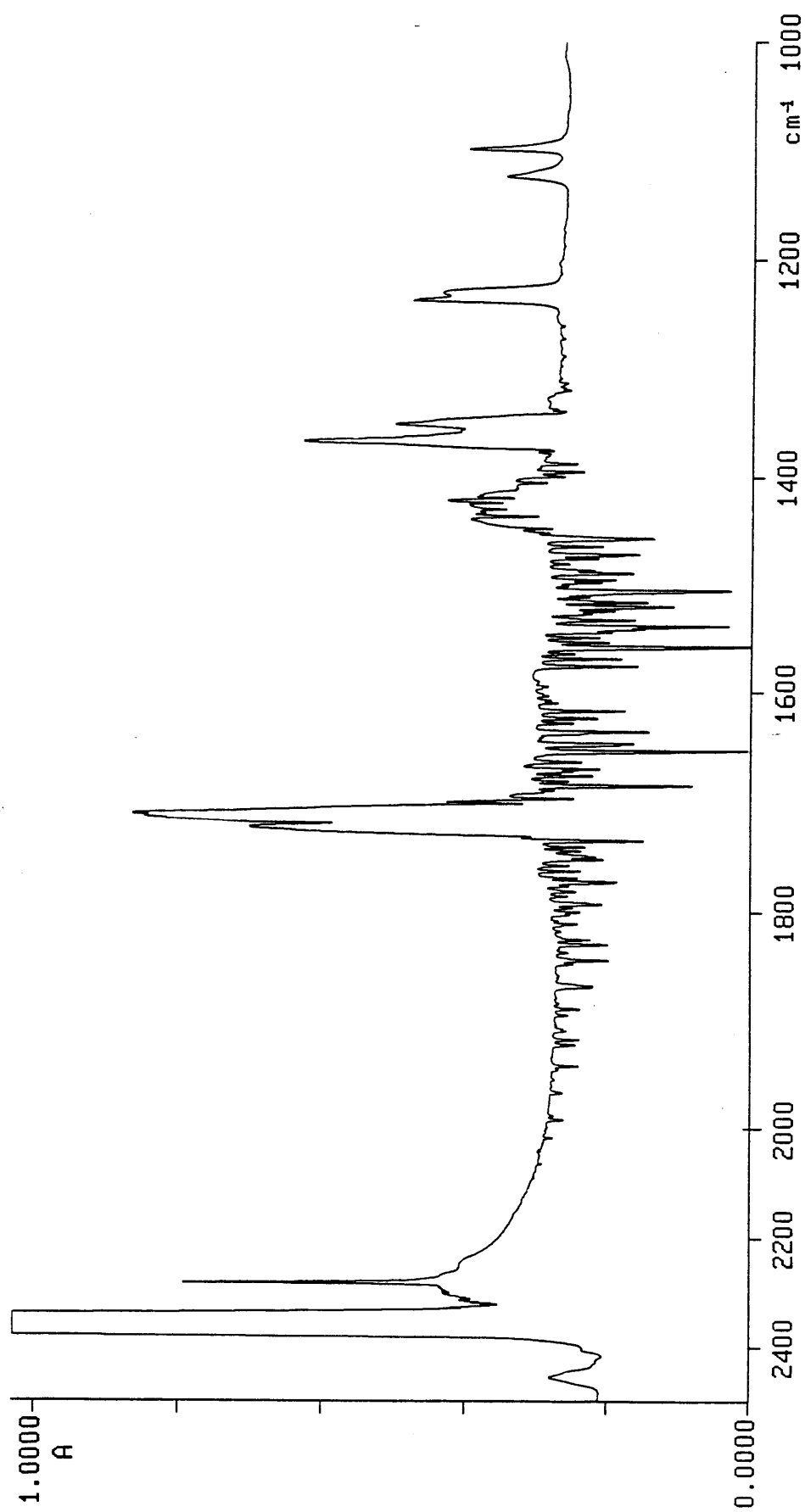


Figure 6.8 (b) IR spectrum of 4:2 mixture of acetone and acetaldehyde in CO₂ matrix after being adsorbed onto a carbon adsorbent tube.
Note lines of water vapour due to poor background subtraction.

Table 6.2: Experimental data for acetone/acetaldehyde mixtures in CO₂ matrix adsorbed onto a carbon tube.

<u>% acetone</u>	<u>% acetaldehyde</u>	<u>MF^a</u>	<u>pk height (A)</u>		<u>Ratio X^b</u>
			<u>acetone</u>	<u>acetaldehyde</u>	
0.00	20.11	0.000	0.000	0.921	0.000
3.55	16.57	0.176	0.284	0.785	0.266
6.82	13.07	0.343	0.416	0.600	0.409
10.84	10.84	0.500	0.545	0.563	0.492
15.44	8.05	0.657	0.688	0.516	0.571
17.05	3.41	0.833	0.729	0.388	0.653
20.08	0.00	1.000	0.821	0.000	1.000

^a Acetone mole fraction

^b Ratio X = (peak height of acetone)/(peak height of acetone + peak height of acetaldehyde)

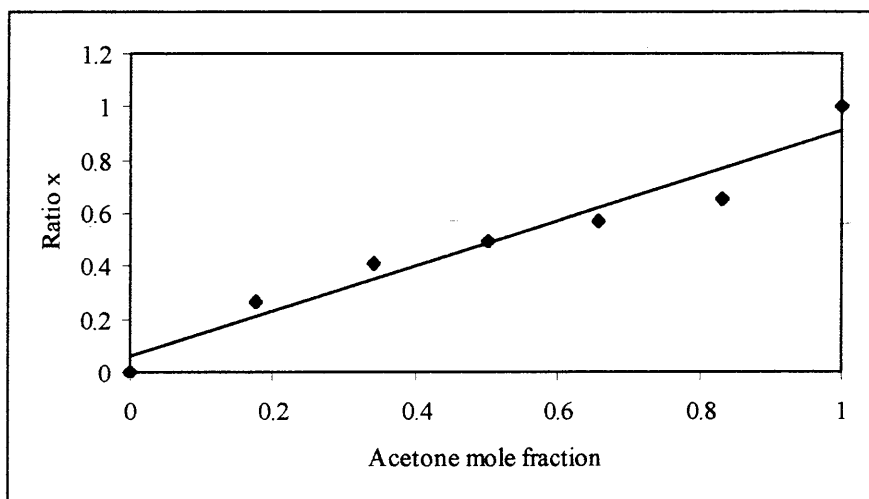


Figure 6.9 The relation between the peak height of the carbonyl absorptions and the acetone mole fraction for mixtures of acetone and acetaldehyde in CO₂ matrices.

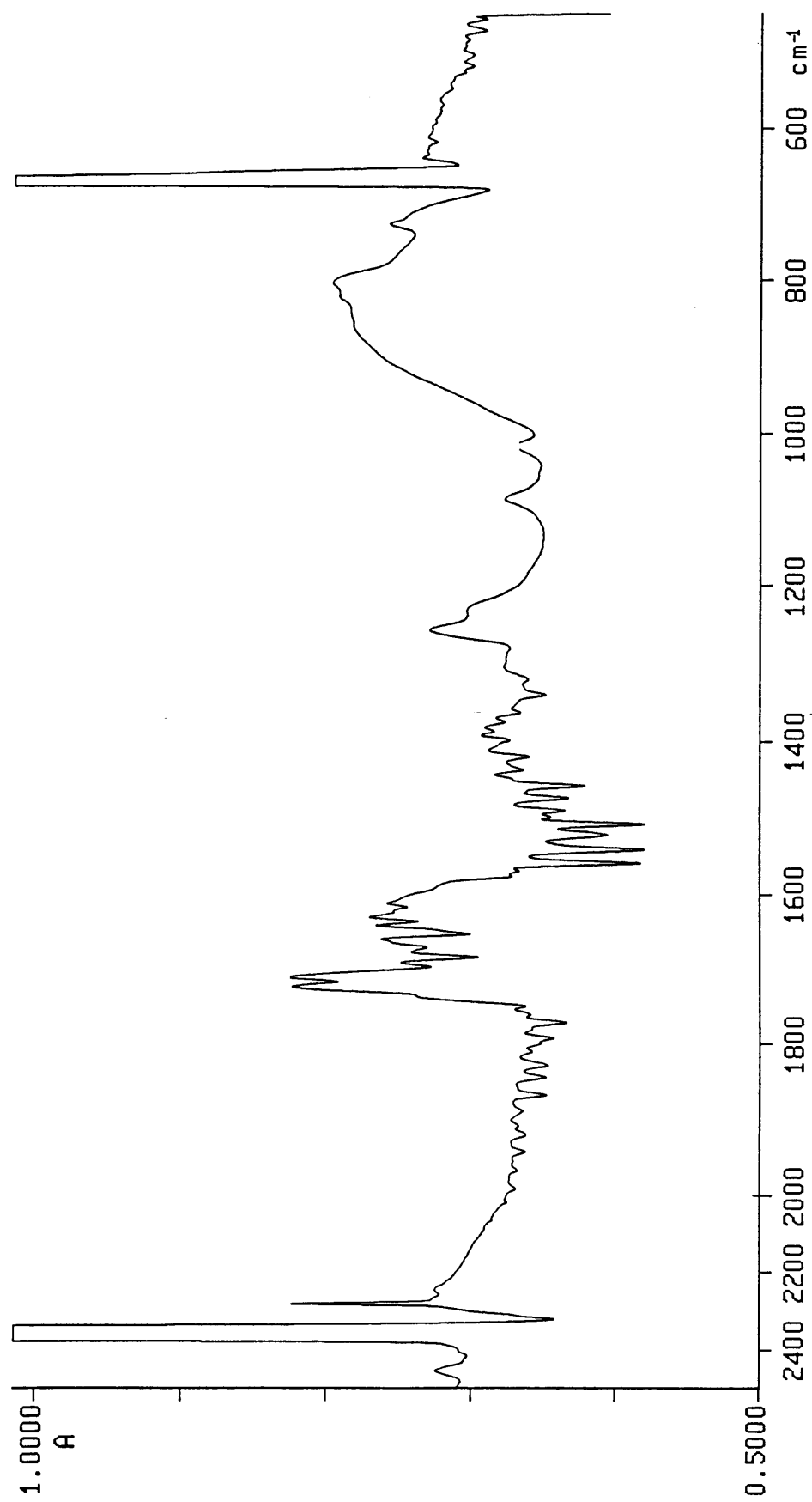


Figure 6.10 IR spectrum of 4:2 mixture of formic acid and acetic acid in CO₂ matrix after being adsorbed onto a carbon adsorbent tube.

cm^{-1} . Also there are another two absorptions that can be used to distinguish between formic acid and acetic acid; the $\nu(\text{C-O})$ absorption of formic acid at about 1080 cm^{-1} and the $\nu(\text{C-O})$ absorption of acetic acid at about 1307 cm^{-1} . The peak heights of the $\nu(\text{C=O})$ absorptions were measured (Table 6.3) and the peak height ratio of formic acid to acetic acid (Ratio X) was calculated for each spectrum and plotted against the formic acid mole fraction (Figure 6.11).

Table 6.3 Experimental data for formic acid/acetic acid mixtures in CO_2 matrix adsorbed onto carbon tubes.

<u>% formic acid</u>	<u>% acetic acid</u>	<u>MF^a</u>	<u>pk height (A)</u>		<u>Ratio X^b</u>
			<u>formic acid</u>	<u>acetic acid</u>	
0.00	12.18	0.000	0.000	0.244	0.000
2.08	10.42	0.166	0.121	0.203	0.373
4.04	8.08	0.333	0.164	0.169	0.492
6.15	6.15	0.500	0.216	0.138	0.610
8.16	4.08	0.667	0.258	0.107	0.707
10.35	2.04	0.835	0.296	0.094	0.759
12.26	0.00	1.000	0.325	0.000	1.000

^a Formic acid mole fraction

^b Ratio X = (peak height of formic acid)/(peak height of formic acid + peak height of acetic acid)

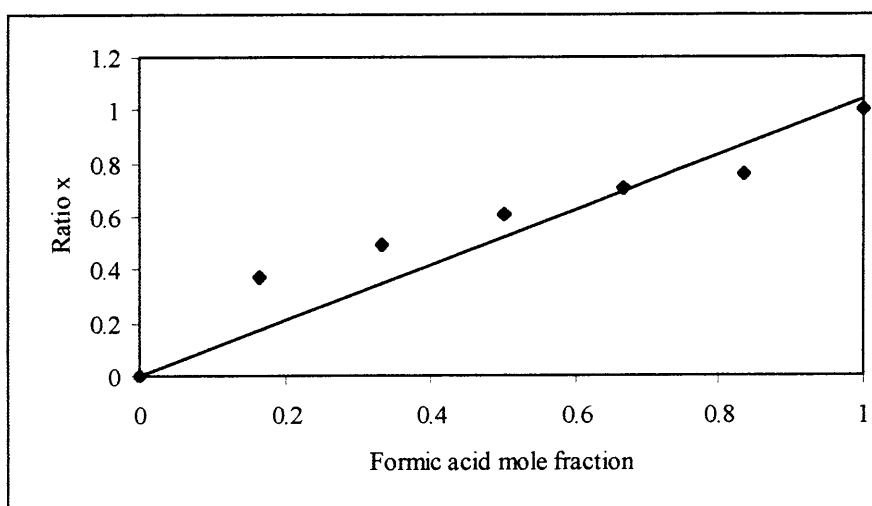


Figure 6.11 The relation between the peak height of the carbonyl absorptions and the formic acid mole fraction for mixtures of formic acid and acetic acid in CO_2 matrices.

The plots of both acetone/acetaldehyde and formic acid/acetic acid mixtures shown linear responses which imply that the presence of one compound does not affect the absorption intensity of other compound, i.e., the compounds can be detected in their real concentration in a gas mixture or in the atmosphere without any interference. This also implies that the activated carbon adsorbent tube can be used successfully in pre-concentrating these atmospheric pollutants.

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Chapter 7 Field Experiments

7.1 Introduction

A particular objective of this research is to monitor the concentrations of carbonyl compounds in the atmosphere. Determination of carbonyl compounds, aldehydes (RCHO), and ketones (R_1COR_2), in the ambient atmosphere is receiving increased attention because of the critical role these compounds play as pollutants and as key participants in tropospheric photochemistry. Carbonyls are involved in photochemical reactions as products of the oxidation of hydrocarbons, precursors of oxidants including ozone and peroxy-carboxylic nitric anhydrides ([PAN]-type compounds), and as sources of free radicals and organic aerosols.

Volatile organic acids ($\text{C}_1\text{-C}_7$), including formic and acetic acids, have been found to be the most abundant species among organic compounds identified in Los Angeles rain.^{1,2} Kawamura *et al.*¹⁻⁴ first identified the presence of significant quantities of low molecular weight mono- and dicarboxylic acids (organic acids) such as formic, acetic and oxalic acids in automobile exhaust. Later Grosjean⁵ estimated the emission rates of organic acids from automobile sources in Los Angeles using Kawamura's data and the concentration ratio of organic acids/carbon monoxide in ambient air and tunnel air.

Organic acids may be emitted by the incomplete combustion of biomass and industrial products in rural and urban environments.⁶ Organic acids may also be directly emitted into the atmosphere from terrestrial plants or through atmospheric oxidation of biogenic hydrocarbons⁶⁻¹⁰ and from stationary sources associated with petrochemical manufacture, plastic manufacture or food manufacture. Organic acids emitted from

automobiles and other sources contribute significantly to the acidification of rain, and they are also involved in the formation of urban smog and haze.

The MI-FTIR technique has been used in this work in combination with the adsorbent tubes for the analysis of multicomponent gas mixtures. The sampling technique provides for high sensitivity and selectivity which recommend this means of analysis. Although this analytical method applies to all infrared absorbing gaseous species, this work is concerned with four carbonyl compounds: acetone, acetaldehyde, acetic acid and formic acid. The main aim is to demonstrate that this sampling technique provides a practicable basis for chemical analysis of these compounds.

7.2 Experimental

7.2.1 Sampling sites and collection method of air samples

Air samples were collected from two sites in Reading, Shinfield Road and the car park in front of the Chemistry Department in Reading University as indicated in the map shown in Figure 7.1. On Shinfield Road, four samples were collected at different times of the day for one hour each sample: from 5:30 to 6:30 a.m., from 8:00 to 9:00 a.m., from 12:00 to 1:00 p.m. and from 5:00 to 6:00 p.m. Air samples were collected from Shinfield Road at the same times in three days. In the car park, samples were collected at three different times of the day: from 9:00 to 10:00 a.m., from 12:00 to 1:00 p.m. and from 4:00 to 5:00 p.m. Air samples were collected from the car park at the same times in three days.

The activated carbon adsorbent tube was chosen to be used for sample collection in the field after being shown to give the best recovery among the four adsorbent

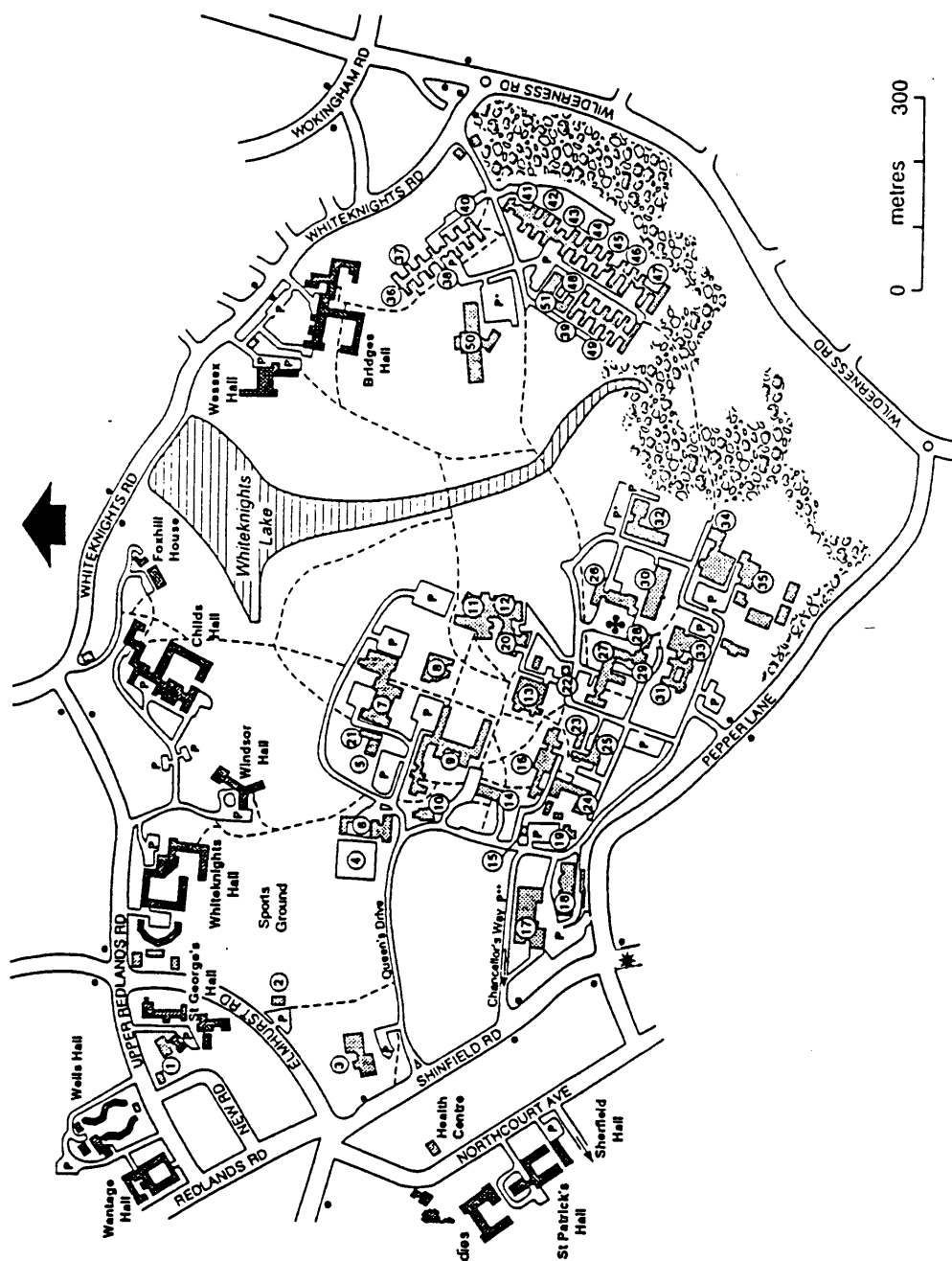


Figure 7.1 A map of the University of Reading campus indicating the sites of the samples collected in the field work.

* Shinfield Road

✦ Chemistry Department car park

materials tested earlier and after being studied for the adsorbent efficiency of acetone/acetaldehyde and formic acid/acetic acid mixtures (see Chapter 6). To check the reproducibility of the sampling technique, triplicate samples of each carbonyl compound in CO₂ were adsorbed onto carbon tubes. The percentage recoveries were calculated as in Table 6.1. The results are shown in Table 7.1. Relative standard deviations to average percentage of recovery are up to 3.2% for individual compound indicating that this method is reproducible.

Table 7.1 Triplicate analysis of the recoveries of carbonyl compounds adsorbed onto carbon tubes.

<u>Sample no.</u>	<u>Acetone</u>	<u>Acetaldehyde</u>	<u>Acetic Acid</u>	<u>Formic Acid</u>
1	90.7	89.6	87.2	88.6
2	87.0	90.6	88.4	90.9
3	85.2	87.5	88.4	87.4
Mean (x)	87.6	89.2	88.0	89.0
SD (Sx)	2.8	1.6	0.7	1.8
Sx/x, %	3.2	1.8	0.8	2.0

In the air sampling, the carbon adsorbent tube was connected to a rotary vacuum pump using rubber tubing and a Young's tap that was kept at the same setting while collecting all the samples to obtain a reproducible volume (Figure 7.2). The sampling was done by switching on the vacuum pump and allowing the air to be drawn through the open end of the tube about 1 m above the ground surface. During the sampling, the adsorbent tube was protected with aluminum foil from sunlight, which may cause photo-oxidation reaction of the trapped material.

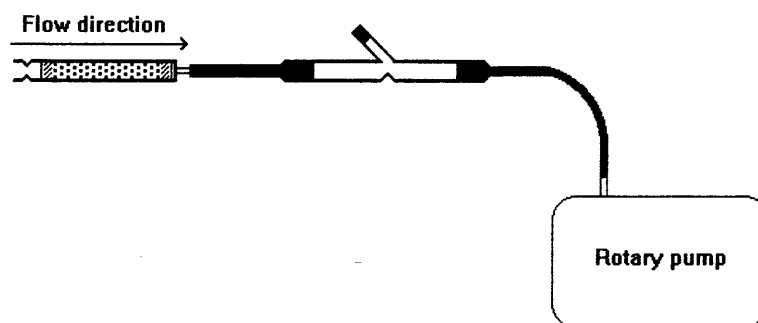


Figure 7.2 The apparatus used for collecting air samples in the field

7.2.2 Sample desorption and analysis

After the air samples were collected into the adsorbent tubes, they were thermally desorbed following the procedure described earlier. After one hour's collection of each sample, the adsorption tube was stoppered and taken to the laboratory for analysis a maximum of 3 hours later. Using rubber tubing, the tube was connected to the deposition point on the cold cell which was connected to the main line. The cell reservoir was filled with liquid nitrogen and the tube was wrapped with the warming tape. After the CsI window reached 77 K the temperature controller on the heater was switched on and set to 80°C. The tap between the tube and the deposition point was opened. After a solid film of the desorbed compounds was formed on the CsI window, the tap was closed, the warming tape and the tube were removed and the IR spectrum was recorded.

7.2.3 Results and analysis of the IR spectra

Of the major classes of organic compounds involved in photochemical air pollution, carbonyls (aldehydes and ketones) are of critical importance as products of the photooxidation of gas-phase hydrocarbons, as a major source of free radicals, and as precursors to organic-aerosol formation in urban air.¹¹

Due to a large extent to analytical difficulties, measurements of ambient levels of carbonyl compounds have been limited to a few urban areas, and in most cases only formaldehyde and/or “total aldehydes” measurements have been performed.

Grosjean *et al.*^{11,12} have performed measurements of ambient levels of carbonyl compounds in the Los Angeles area. In their study, they used a 2,4-dinitrophenylhydrazine (DNPH) reagent which reacts with carbonyl compounds to form 2,4-dinitrophenylhydrazones. The hydrazones are separated by high-pressure liquid chromatography (HPLC) and quantitated on the basis of their absorption at 360 nm. From their study, they found the concentrations to be up to 48 ppb for formaldehyde and ≤ 35 ppb for acetaldehyde.

Atmospheric organic acids were first reported in down-town Los Angeles by using a bubbler filled with NaOH solution to trap the acids followed by separation using silica gel column chromatography-titration.¹³ The concentration of formic acid ranged from 0.0 to 0.41 ppm, but that of acetic acid was not described. FTIR spectroscopy (but not involving matrix isolation methods) has been applied by other researchers^{14,15} to measure atmospheric pollutants, and formic acid has been reported at levels of 0-19 ppb in the Los Angeles area. Ion chromatography has been also used for measuring formic and acetic acids in the atmosphere of Tuscon, Arizona, after collection with water films.¹⁶ The reported concentrations were 1-6 ppb. Activated charcoal trapping followed

by high-pressure liquid chromatography (HPLC) analysis has been used for the determination of formic acid in air samples.¹⁷

Kawamura *et al.*³ described a gas chromatography method for the determination of volatile organic acids (C₁-C₁₀) in the atmosphere and motor exhaust which were trapped on an alkaline-treated quartz-fiber filter. The concentrations of formic acid in the atmosphere were 0.07-3.0 ppb and those of acetic acid were 0.26-3.9 ppb. In motor exhaust, formic acid was found to be 9.30 ppb and acetic acid was 31.81 ppb.

The technique of analysis used in this work requires that a standard spectrum be recorded for each chemical species of interest. This has been done for the four compounds in Chapter 4 namely acetone, acetaldehyde, formic acid and acetic acid and the IR spectra are shown in Figures 4.2, 4.3, 4.6 and 4.11, respectively. Carbonyl compounds in the samples were identified by comparing the spectra of the air samples with those of the standards. Analysis of the IR spectra of the standards appear in Table 7.2, where actual observed frequencies, intensities, and bandwidths are listed. Only absorptions with absorbances of 0.03 or greater are recorded. The intensities indicated are not normalized.

7.2.3.1 Air samples from Shinfield Road

Figures 7.3-7.9 provide several examples of recorded spectra illustrating the specificity of this technique. Figure 7.3 shows the IR spectrum of the air sample that was collected from Shinfield Road on 19/3/1998 between 5:30 and 6:30 a.m. Only absorptions of water (at about 3227 and 1640 cm⁻¹) and CO₂ (at about 2360, 2280 and 666 cm⁻¹) are observed for this sample implying that the air does not contain a significant amount of pollutants that can be detected at that time of the day. Figure 7.4

Table 7.2 Characteristic spectra for some carbonyl compounds in CO₂ matrices.

<u>Compound</u>	<u>ν (cm⁻¹)</u>	<u>Absorbance</u>	<u>Δ^1</u>
Acetone	3228.0	0.141	59.7
	1711.1	0.562	14.6
	1441.8	0.058	35.5
	1420.5	0.064	36.5
	1365.7	0.270	17.7
	1229.5	0.181	14.7
	1095.9	0.041	8.1
	534.5	0.074	8.2
Acetaldehyde	3226.8	0.184	76.4
	2867.2	0.085	24.8
	2767.6	0.076	31.6
	1723.1	1.488	9.4
	1436.5	0.250	16.3
	1350.5	0.382	8.6
	1123.2	0.259	8.1
	887.9	0.042	20.4
	772.1	0.029	15.6
	518.3	0.239	7.8
Acetic Acid	2923.6	0.151	310.7
	1715.2	0.537	30.2
	1412.9	0.109	49.4
	1362.8	0.089	17.8
	1307.9	0.267	26.6
	1051.4	0.028	13.5
	1020.3	0.056	18.6
	951.6	0.067	64.1
	635.9	0.058	12.6
Formic Acid	489.0	0.049	13.2
	2902.8	0.065	116.2
	2752.2	0.052	108.4
	2585.3	0.078	83.6
	1712.1	0.253	42.4
	1609.9	0.104	51.5
	1391.4	0.052	22.9
	1260.1	0.156	28.8
	1224.6	0.076	0
	1083.4	0.072	38.7
	1016.1	0.061	104.2
	954.6	0.046	175.5
	799.0	0.072	31.6
	727.2	0.050	14.8
	663.9	0.423	15.1

¹ Full width at half height (cm⁻¹).

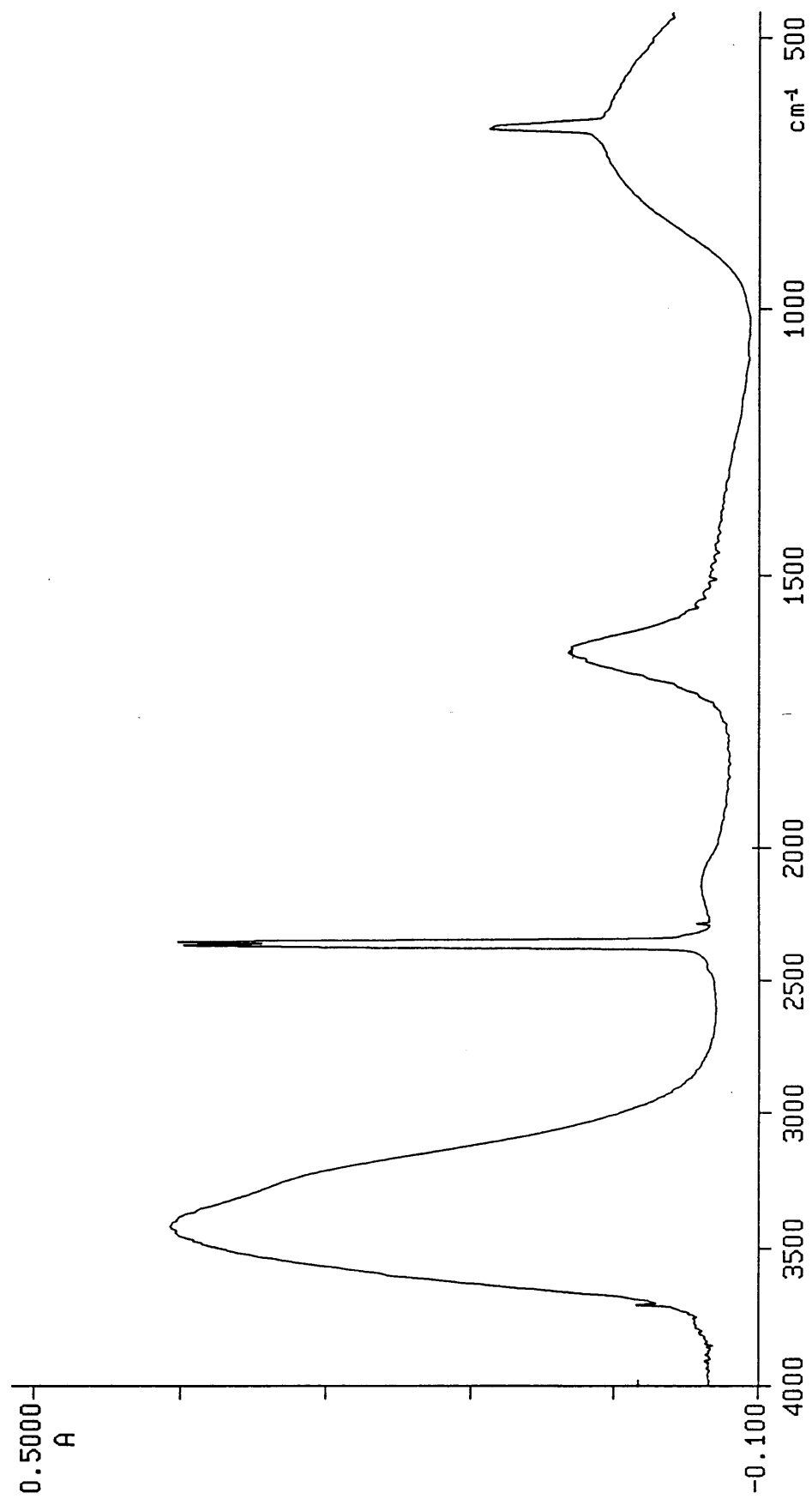


Figure 7.3 IR spectrum of the air sample collected from Shinfield Road on 19/3/1998 (5:30-6:30 a.m.)

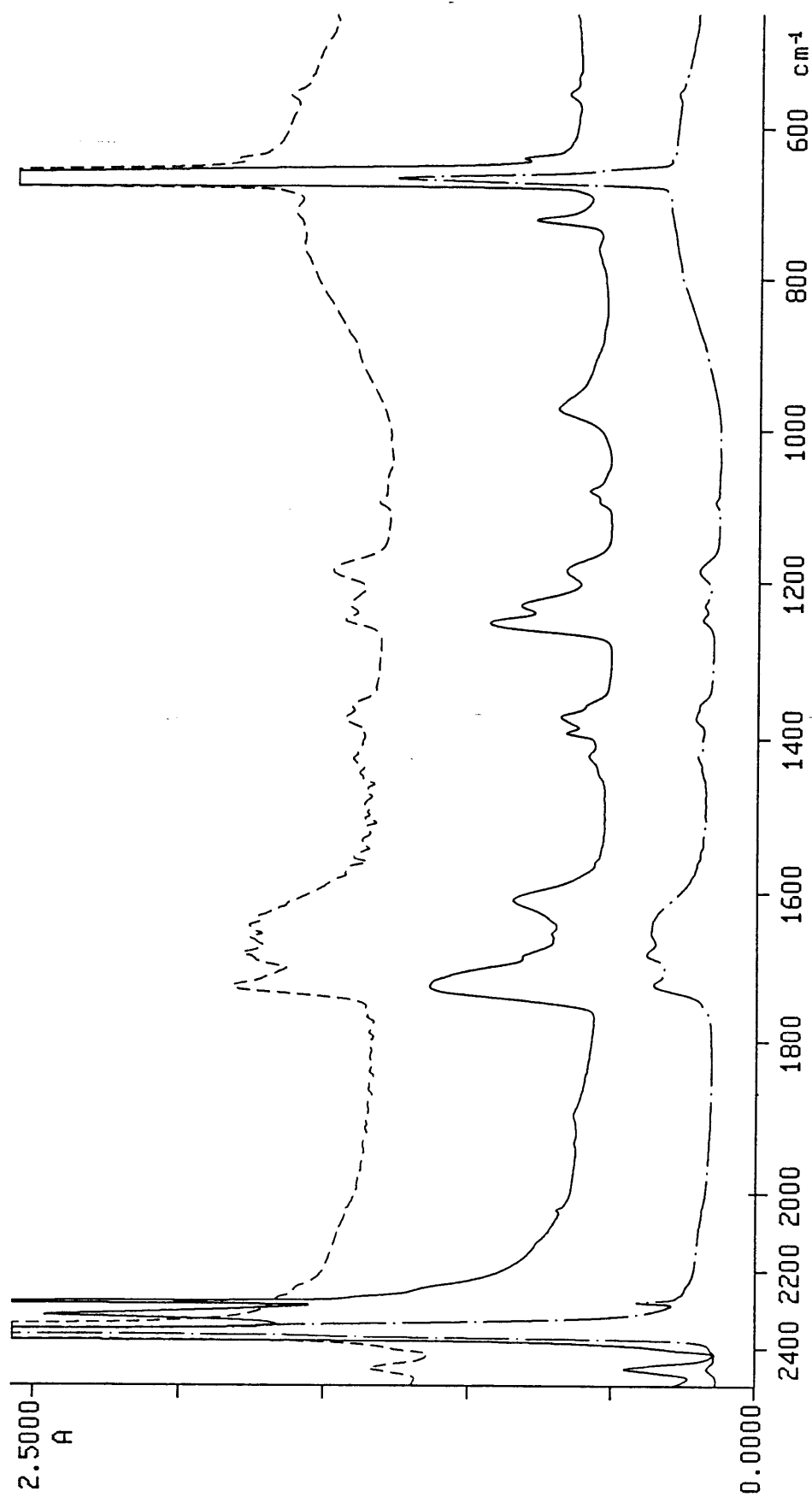


Figure 7.4 IR spectra of the air samples collected from Shinfield Road on 19/3/1998
— (8:00-9:00 a.m.)
- · - (12:00-1:00 p.m.)
--- (5:00-6:00 p.m.)

corresponds to the spectra of the three samples collected later on the same day. The spectra show that each sample contains some of the studied carbonyl compounds. The frequencies are widely separated; thus, tentative identification and semi-quantitative measures of each compound may be achieved. Spectrum (a) is for the sample collected between 8:00 and 9:00 a.m. when the traffic was at its peak. Many absorptions are observed in this spectrum indicating the presence of different organic compounds which are produced by the car exhaust into the air. There are three bands at 2898.5, 2742 and 2577 cm^{-1} and a single band at 1609.5 cm^{-1} which are characteristic of formic acid. The presence of these bands at the appointed frequencies establishes the presence of formic acid in the sample. A band at 1422 cm^{-1} in the spectrum of the same sample is characteristic for acetone. Other bands are assigned to acetone such as those at 1371.5 cm^{-1} and 555 cm^{-1} . The bands that imply the presence of acetaldehyde in the sample are those at 759 cm^{-1} and 1725 cm^{-1} . The assignment of these bands and other bands are listed in Table 7.3. Other organic compounds are undoubtedly present in this sample but since the standard IR spectra of only the four studied compounds, i.e., acetone, acetaldehyde, acetic acid and formic acid, are available, it is not possible definitively to assign any other compound. In Table 7.3 the IR spectra of the air samples are compared with the spectra observed for each of the studied compounds and assignments are made. Because of the complex mixture of compounds in the atmospheric samples assignments were made allowing a frequency difference of $\pm 10 \text{ cm}^{-1}$ from the spectra of the standard compounds.

Spectrum (b) is for the sample collected when the traffic was less crowded between 12:00 and 1:00 p.m. The intensities of most of the absorptions observed in spectrum (a) have decreased in spectrum (b) but some new absorptions are observed indicating the formation of new compounds with time as products of chemical or

Table 7.3 Analysis of the IR spectra of the air samples collected from Shinfield Road on 19/3/1998.

08:00-09:00			12:00-13:00			17:00-18:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
2898.5	0.107	FA	3416.2					
2742.2	0.107	FA	2710.0	0.018	FA	2742.3	0.032	FA
2577.3	0.214	FA	2580.0	0.014	FA	2578.7	0.054	FA
2454.9	0.268		2454.2	0.032		2454.4	0.182	
2280.0	2.996	CO ₂	2281.4	0.259	CO ₂	2281.7	0.657	CO ₂
1897.5								
1725.3	0.574	Acetaldehyde	1723.3	0.191	Acetaldehyde	1724.9	0.492	Acetaldehyde
1609.5	0.286	FA	1682.9	0.223		1680.7	0.435	
			1653.6	0.207		1643.1	0.434	
						1442.9		Acetone
1421.9	0.056	Acetone	1422.5	0.024	Acetone	1425.1	0.065	Acetone
1392.1	0.135	FA	1373.8	0.032	Acetone	1373.7	0.107	Acetone
						1359.3	0.075	
1371.5	0.158	Acetone	1247.2	0.039	FA	1247.3	0.124	FA
1251.5	0.425	FA	1229.2	0.033	FA	1227.9	0.110	FA
1229.0	0.318	FA	1184.6	0.050		1183.6	0.190	
1184.4	0.158							
1094.7	0.043		1095.8	0.014	Acetone	1095.4	0.037	Acetone
1080.1	0.075	FA						
970.4	0.183	FA						
759.3		Acetaldehyde				757.9		
720.9	0.195	FA				708.7		FA
554.9	0.038	Acetone	555.0	0.014	Acetone	555.2	0.043	Acetone

photochemical reactions. Again only the presence of the studied carbonyl compounds can be definitely confirmed as the spectra of these standard compounds are available for comparison. Two high frequency bands are observed at 2710 and 2580 cm^{-1} and can be assigned to formic acid. A third band which is observed at 2903 cm^{-1} in the standard spectrum of formic acid is not observed in the sample spectrum (b) but the presence of the two high frequency bands along with the band at 1229 cm^{-1} is enough to establish the presence of formic acid in this sample. By comparing spectrum (b) to the data in Table 7.2, bands of acetone can be assigned as well, such as those at 1422.5, 1374, 1096 and 555 cm^{-1} . The presence of acetaldehyde in the sample is indicated by the absorption at 1723 cm^{-1} . New absorptions at 1683 and 1654 cm^{-1} are observed in this sample and they cannot be assigned to any of the studied compounds as there are no corresponding absorptions in the spectra of the standard compounds listed in Table 7.2.

Spectrum (c) is for the sample collected when the traffic was crowded again between 5:00 and 6:00 p.m. It is more similar to spectrum (b) than to spectrum (a) with higher intensities of most of the absorptions. The presence of formic acid in the sample is indicated by the presence of the two bands at 2742 and 2579 cm^{-1} , and also by the presence of the bands at 1247 and 1228 cm^{-1} . The presence of acetone in the sample is indicated by the absorptions at 1425, 1374, 1095 and 555 cm^{-1} . A new absorption at 1443 cm^{-1} is observed which is assigned to acetone. The presence of acetaldehyde in the sample can only be inferred from the presence of the absorption at 1725 cm^{-1} which is assigned to the $\nu(\text{C}=\text{O})$ stretching vibration.

In Figures 7.5 and 7.6 are shown the IR spectra of the samples collected from Shinfield Road on 20/3/1998 and 23/3/1998, respectively. The general observations from these two sets of spectra is that the second set of spectra are very similar to the first one. These spectra were analysed and the absorptions were compared with those of

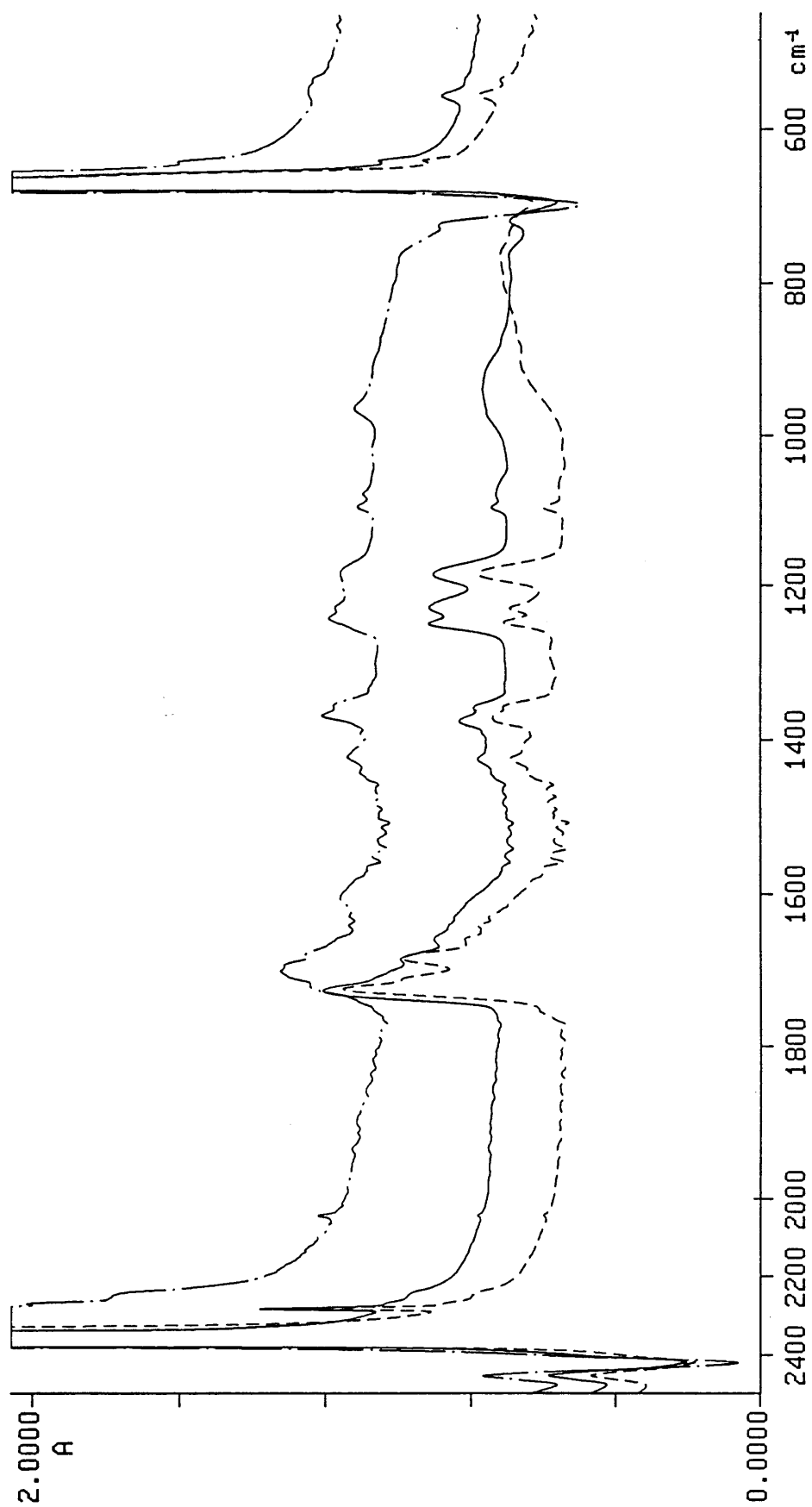


Figure 7.5 IR spectra of the air samples collected from Shinfield Road on 20/3/1998

— (8:00-9:00 a.m.)
- - - (12:00-1:00 p.m.)
- . - (5:00-6:00 p.m.)

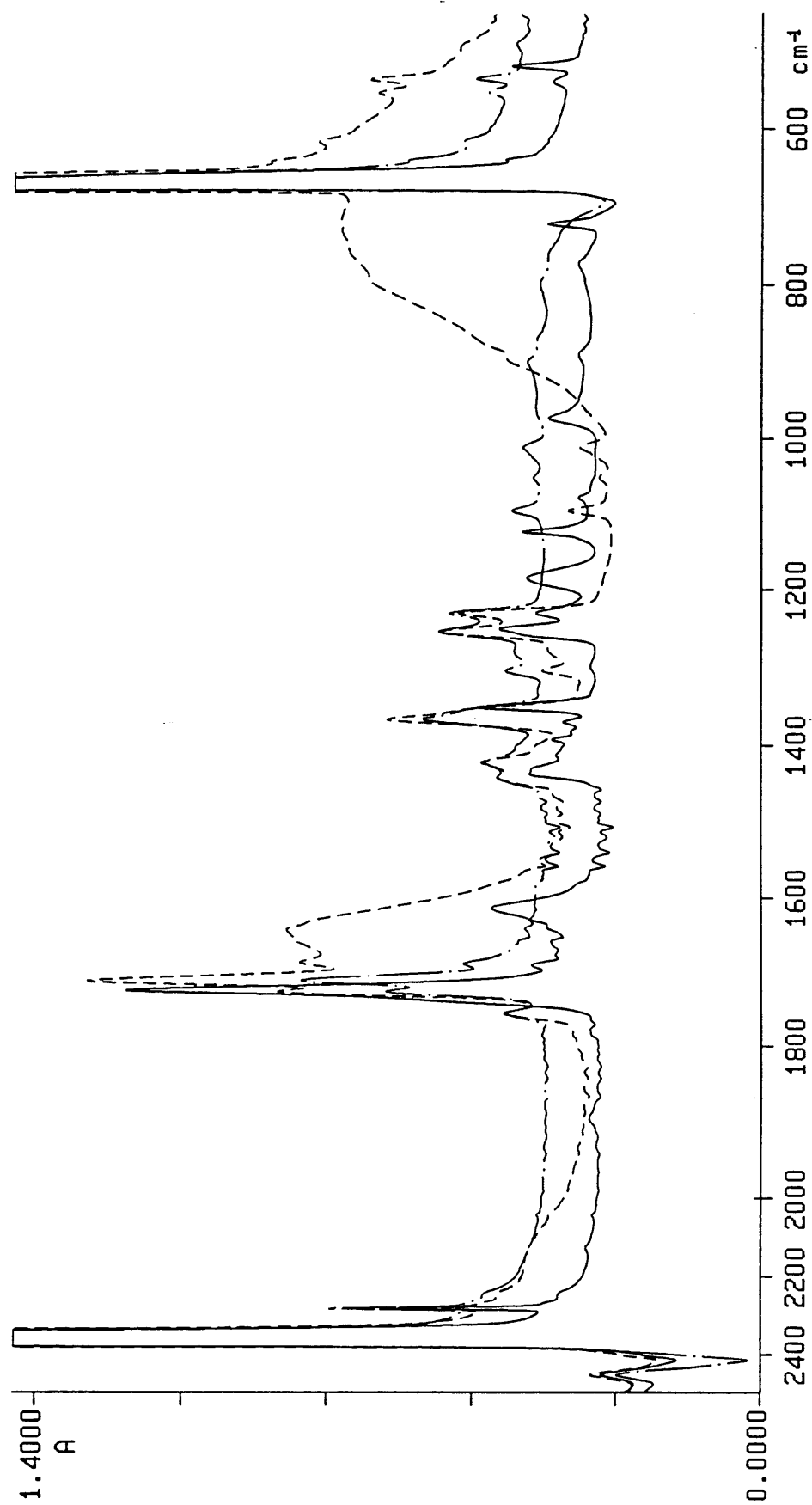


Figure 7.6 IR spectra of the air samples collected from Shinfield Road on 23/3/1998

— (8:00-9:00 a.m.)
- - - (12:00-1:00 p.m.)
- . - (5:00-6:00 p.m.)

the standard compounds listed in Table 7.2 and the results of the qualitative analysis are shown in Tables 7.4 and 7.5. In Tables 7.3-7.5 is provided a compilation of all bands listed in Table 7.2 sequenced according to frequency. Where intensity entries are omitted, the respective bands were found to have an absorbance less than 0.03. The unassigned frequencies are those which were not identified as one of the four carbonyl compounds under investigation, i.e., acetone, acetaldehyde, formic acid or acetic acid. The data provided in Table 7.5 show that the spectra shown in Figure 7.6 have more absorption bands than the other two sets of spectra (Figures 7.4 and 7.5). Also more bands are assigned to acetaldehyde in this set than in the previous two sets suggesting a higher concentration of acetaldehyde in these samples.

6.2.3.2 Air samples from the car park

In Figure 7.7 is shown the IR spectra of three air samples collected from the car park in front of the Chemistry Department on 24/3/1998. The spectra show that each of the three samples contains one or more of the studied carbonyl compounds in different concentrations. The spectra were analysed and the absorptions were compared with those of the standard compounds listed in Table 7.2. The qualitative analyses of these spectra is given in Table 7.6. Spectrum (a) is for the sample collected between 9:00 and 10:00 a.m. The band at 1696 cm^{-1} is assigned to acetone. The presence of formic acid is indicated by the presence of the bands at 1717, 1258, 1077, 943 and 799 cm^{-1} . The presence of any of these bands is enough to establish the presence of formic acid in the sample. The band occurs at 1437 cm^{-1} is characteristic for acetaldehyde. Another band assigned to acetaldehyde is at 1115 cm^{-1} .

Table 7.4 Analysis of the IR spectra of the air samples collected from Shinfield Road on 20/3/1998.

08:00-09:00			12:00-13:00			17:00-18:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
2935.1	0.086	FA	2932.3	0.043	FA			
2744.9	0.075	FA	2706.5	0.043		2708.0	0.043	FA
2576.4	0.139	FA				2585.5	0.064	
2454.6	0.268		2455.3	0.246		2454.6	0.214	
2281.8	0.638	CO ₂	2280.8	3.550	CO ₂	2281.6	0.789	CO ₂
2040.7			2041.9	0.043				
			1720.2	0.214				
1726.1	0.489	Acetaldehyde	1700.3	0.292	Acetone	1724.3	0.609	Acetaldehyde
1686.5	0.279		1676.9	0.225				
1659.2	0.183		1604.2	0.125	FA	1684.4	0.448	
1441.1	0.043		1441.1	0.054		1441.1	0.086	
1423.8	0.069	Acetone	1420.7	0.084	Acetone	1423.6	0.106	Acetone
1375.4	0.121	Acetone	1367.5	0.149	Acetone	1370.7	0.155	Acetone
1354.5	0.096		1354.5	0.129		1357.8	0.150	
1248.6	0.210	FA	1241.0	0.118	FA	1246.9	0.134	FA
1227.7	0.209	FA	1227.0	0.107		1228.8	0.117	FA
1183.9	0.198		1182.4	0.088		1183.4	0.205	
1095.2	0.042	Acetone	1093.6	0.043	Acetone	1095.5	0.051	Acetone
1077.1	0.032		1076.6	0.032				
937.5	0.066	FA	962.4	0.057	FA			
757.9								
718.2		FA				762.3		Acetaldehyde
555.4	0.048	Acetone	543.1	0.032		554.5	0.045	acetone

Table 7.5 Analysis of the IR spectra of the air samples collected from Shinfield Road on 23/3/1998.

08:00-09:00			12:00-13:00			17:00-18:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
3005.2	0.043		3005.7					
2896.4	0.064	FA						
2753.9	0.071	FA						
2544.9	0.121	FA						
2454.3	0.100		2454.7	0.143		2454.5		
2281.6	0.396	CO ₂	2281.8	0.388	CO ₂	2281.8	0.501	CO ₂
1894.9			1755.8	0.073		1755.6	0.148	
1723.5	0.912	Acetaldehyde	1726.0	0.309	Acetaldehyde	1725.7	0.589	Acetaldehyde
1690.2	0.132		1710.7	0.470	Acetone	1710.5	0.955	Acetone
1658.3	0.100		1688.3	0.157		1685.7	0.543	
1613.1	0.211	FA	1640.7			1641.7	0.570	
1435.9	0.137	Acetaldehyde	1440.0	0.086	Acetone	1440.2	0.121	Acetone
1392.0	0.087	FA	1421.2	0.114	Acetone	1421.1	0.155	Acetone
1369.1	0.071	Acetone	1365.5	0.223	Acetone	1365.7	0.370	Acetone
1350.5	0.241	Acetaldehyde						
1300.0		AA	1304.1	0.066	AA	1304.0	0.073	AA
1249.7	0.187	FA	1252.7	0.196	FA	1253.0	0.305	FA
1229.8	0.117	FA	1229.1	0.180	FA	1229.2	0.272	FA
1183.8	0.132							
1123.2	0.139	Acetaldehyde	1095.3	0.050	Acetone	1095.5	0.083	Acetone
1078.2	0.034	FA	1051.8		AA	1051.7		AA
972.1	0.093	FA	1011.1	0.039	AA	1011.0	0.053	AA
888.5		Acetaldehyde	898.9		Acetaldehyde			
772.2	0.023	Acetaldehyde	797.8		FA			
721.3	0.094	FA						
538.1	0.026	Acetone	551.2	0.028	Acetone	551.7	0.054	Acetone
518.3	0.105	Acetaldehyde	534.0	0.053	Acetone	534.4	0.107	Acetone

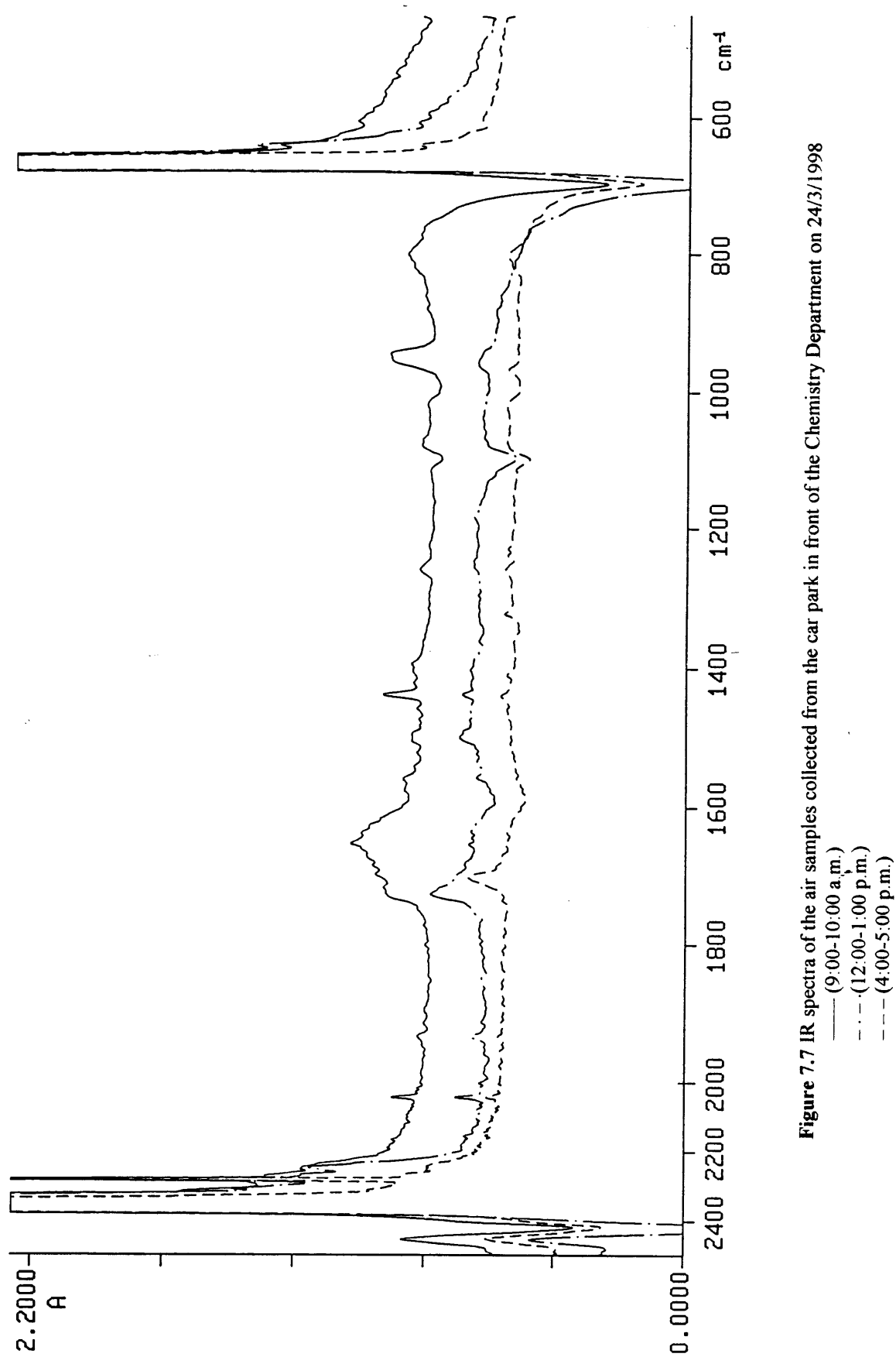


Figure 7.7 IR spectra of the air samples collected from the car park in front of the Chemistry Department on 24/3/1998
— (9:00-10:00 a.m.)
- - - (12:00-1:00 p.m.)
· · · (4:00-5:00 p.m.)

Table 7.6 Analysis of the IR spectra of the air samples collected from the car park in front of the Chemistry Department on 24/3/1998.

09:00-10:00			12:00-13:00			16:00-17:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
2454.4	0.707		2455.4	0.267		2453.2	0.288	
2281.5	1.572	CO ₂	2281.3	2.069	CO ₂	2281.9	1.785	CO ₂
2041.4	0.097		2041.8	0.094		2042.4	0.052	
1933.3	0.027		1934.2	0.047				
1716.8	0.145	FA	1726.0	0.168	Acetaldehyde	1701.9	0.128	Acetone
1696.0	0.167	Acetone	1653.8					
1652.3	0.254							
1559.0	0.038		1557.5	0.036				
1494.6	0.025		1499.7	0.060				
1456.4								
1436.9	0.128	Acetaldehyde	1436.9	0.036	Acetaldehyde	1465.0		
1393.1						1439.7	0.035	Acetaldehyde
						1409.2		
						1322.0	0.049	
						1261.0	0.028	FA
1257.8	0.040	FA	1246.1	0.016	Acetone	1238.7		Acetone
1115.1	0.065	Acetaldehyde	1182.4	0.015		1072.7	0.043	
1077.3	0.096	FA	1036.5		AA	1023.6	0.043	AA
1017.4	0.043							
942.6	0.165	FA	956.3	0.035	FA	966.2	0.037	FA
						877.9		
799.0	0.085	FA				805.4	0.042	

Spectrum (b) is for the sample collected between 12:00 and 1:00 p.m. from the car park on the same day. The intensities of most of the absorptions have decreased in this spectrum. Most of the absorptions have the same frequencies as in spectrum (a). Few absorptions appear in this spectrum which are not observed in the spectrum of the first sample. An exception is the absorption at 1726 cm^{-1} which can be assigned to the $\nu(\text{C}=\text{O})$ stretching vibration of acetaldehyde which only appears in the sample collected between 12:00 and 1:00 p.m. Another absorption which indicates the presence of acetaldehyde is the one at 1437 cm^{-1} . Another new absorption is the one at 1037 cm^{-1} which can be assigned to acetic acid or perhaps to other organic compounds present in the sample. Some of the absorptions have not been assigned as there are no corresponding absorptions in the spectra of the studied compounds listed in Table 7.2. The only absorption that indicates the presence of formic acid in the sample is the one appears at 956 cm^{-1} .

Spectrum (c) is for the sample collected between 4:00 and 5:00 p.m. from the car park on the same day. Most of the absorptions have similar frequencies to those in the two previous spectra. The most obvious difference is the position of the carbonyl absorption. In this spectrum the $\nu(\text{C}=\text{O})$ stretching vibration appears at 1702 cm^{-1} and can be assigned to acetone. The change in the position of the carbonyl group absorption in these spectra implies that more than one carbonyl compound is present in the sample and that some chemical reactions are taking place with time that can cause the presence of different compounds in each sample. Also the concentrations of some compounds in the sample may affect the nature of the reaction products and therefore the position of some absorptions. Another band that indicates the presence of acetone in this sample is the one at 1239 cm^{-1} . The presence of acetic acid in this sample is indicated by the band

at 1024 cm^{-1} only. Acetaldehyde is indicated by the band at 1440 cm^{-1} only and formic acid is indicated by the bands at 1261 and 966 cm^{-1} .

In Figures 7.8 and 7.9 are shown the IR spectra of the samples collected from the car park in front of the Chemistry department on 20/5/1998 and 21/5/1998, respectively, and their qualitative analyses are given in Tables 7.7 and 7.8. In general, more absorption bands appear in these two sets of spectra than in the first set shown in Figure 7.7. The reason is that the last two sets of samples have been collected at a different time of the year when it was sunny and the temperatures were higher ($15\text{--}18^\circ\text{C}$ in May vs. $7\text{--}9^\circ\text{C}$ in March). This may cause more photochemical reactions to take place and the products to accumulate as it was also less windy. Another observation is that in all the spectra of the samples collected from the car park there is one or more bands assigned to acetic acid while there is no absorption assigned to acetic acid in any of the spectra of the samples collected from Shinfield Road. This is probably because different sites of sampling have different chemical compounds depending on the sources of these compounds. In all the spectra of the air samples a band of CO_2 appears at $2281.3 \pm 0.3\text{ cm}^{-1}$ with a relatively high intensity. It corresponds to the asymmetric stretch of the isotopomer $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ that is chosen as an internal standard and can be used in the quantitative analysis of the carbonyl compounds in the samples (see Section 3.6).

With regard to the recording of standard spectra, entire spectra need not be collected in catalogue fashion. Rather, a table of selected characteristic frequencies should be composed from information similar to that recorded in Tables 7.2-7.8. Tables 7.3-7.8 are used to select frequencies which are suitably isolated. An example of such a compilation is provided by Table 7.9. After the presence of a compound has been established, a single frequency is sufficient for this purpose, Tables 7.2-7.8 may be used to identify other bands in the spectrum.

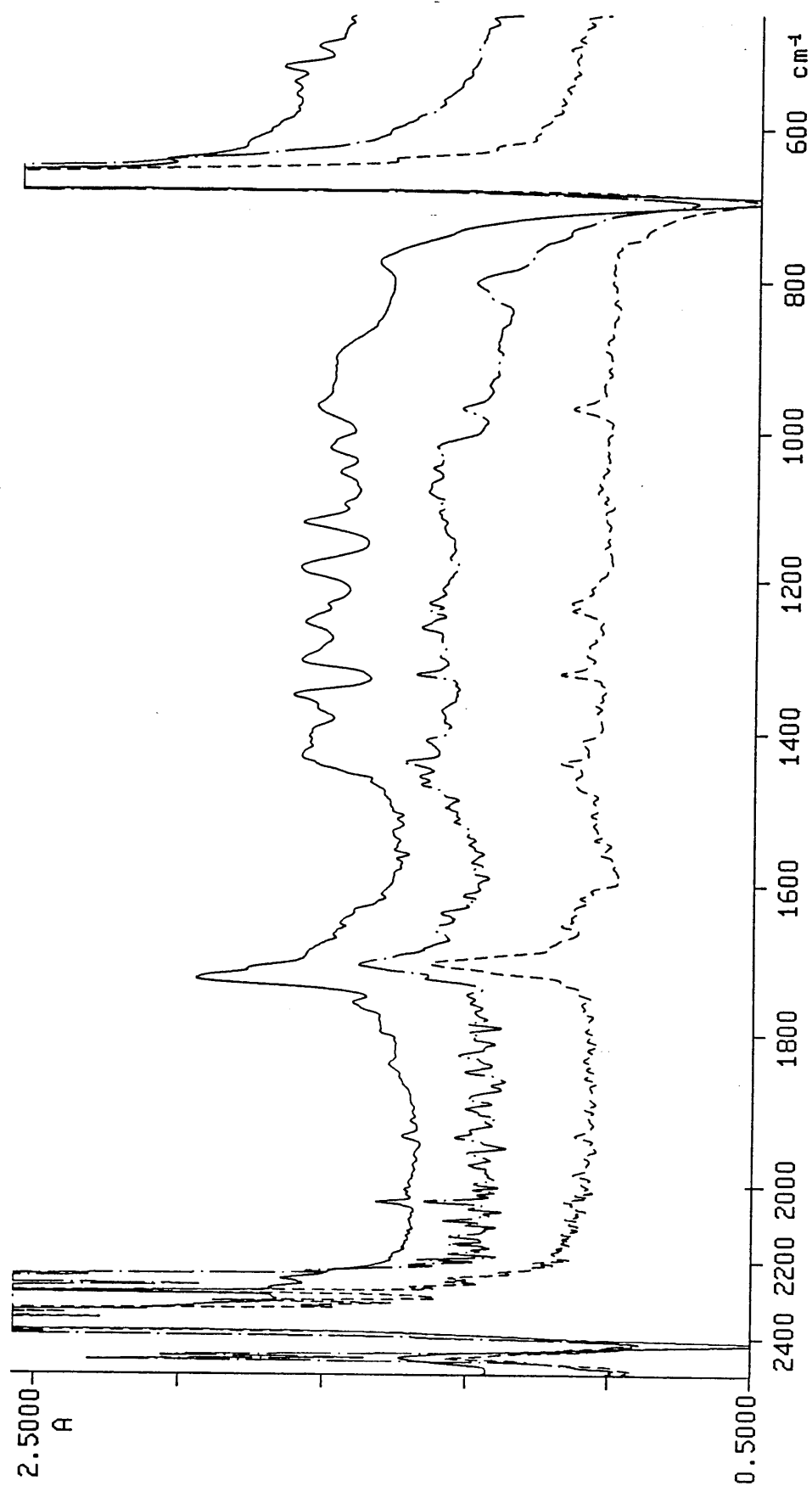


Figure 7.8 IR spectra of the air samples collected from the car park in front of the Chemistry Department on 20/5/1998

— (9:00-10:00 a.m.)
- - - (12:00-1:00 p.m.)
· · · (4:00-5:00 p.m.)

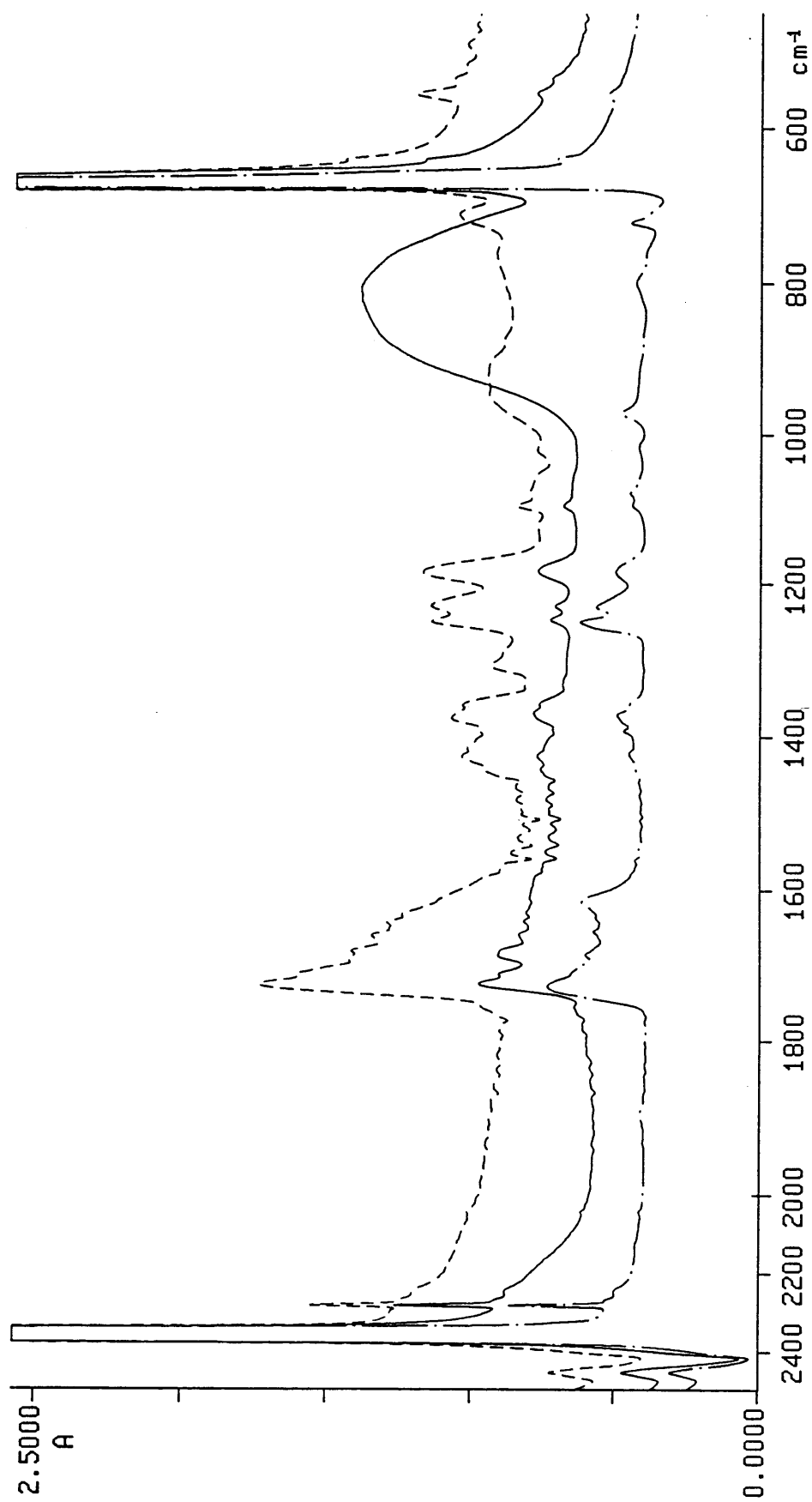


Figure 7.9 IR spectra of the air samples collected from the car park in front of the Chemistry Department on 21/5/1998
— (9:00-10:00 a.m.)
- · - (12:00-1:00 p.m.)
--- (4:00-5:00 p.m.)

Table 7.7 Analysis of the IR spectra of the air samples collected from the car park in front of the Chemistry Department on 20/5/1998.

09:00-10:00			12:00-13:00			16:00-17:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
2640.1	0.080	FA						
2578.7	0.080	FA						
2455.4	0.505							
2281.9	1.198	CO ₂	2449.0	1.203		2456.4	0.513	
2041.8	0.107		2280.7	4.509	CO ₂	2280.4	1.755	CO ₂
1933.9	0.051		2040.7	0.200		1984.8		
1839.0			1935.9	0.096		1933.8		
1756.1	0.075		1724.3	0.162	Acetaldehyde	1704.2	0.460	Acetone
1724.3	0.568	Acetaldehyde	1705.8	0.332	Acetone			
1649.4								
1529.5			1656.6	0.148		1653.6		
1430.0	0.214	Acetaldehyde				1465.0		
1349.7	0.213	Acetone	1437.5	0.152	Acetaldehyde	1438.5	0.114	Acetaldehyde
1304.4	0.190	AA	1409.0	0.064	AA	1411.0	0.061	AA
1253.4	0.125	FA	1322.7	0.113		1322.3	0.130	
1181.1	0.174		1260.6	0.056	FA	1297.3		AA
1121.0	0.157	Acetaldehyde				1228.9	0.089	Acetone
1096.6	0.043	Acetone	1107.1					
1052.8	0.048	AA	1079.8	0.042	FA			
1019.6	0.076	AA						
962.9	0.107	FA	967.1	0.065	FA			
773.3		Acetaldehyde	800.6	0.101	FA	967.3	0.111	FA
518.0		Acetaldehyde						
490.7		AA	454.5			559.6		

Table 7.8 Analysis of the IR spectra of the air samples collected from the car park in front of the Chemistry Department on 21/5/1998.

09:00-10:00			12:00-13:00			16:00-17:00		
ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound	ν (cm ⁻¹)	A	compound
2454.9			2960.0	0.043	FA	2950.0	0.064	FA
2281.0	0.692	CO ₂	2736.2	0.054	FA	2741.8	0.054	FA
			2554.8	0.129	FA	2578.0	0.171	FA
			2454.9	0.164		2455.0		
			2281.0	0.469	CO ₂	2281.7	0.590	CO ₂
			1896.8					
1723.5	0.340	Acetaldehyde	1726.6	0.344	FA	1723.6	0.856	Acetaldehyde
1685.6	0.274		1685.0	0.208		1680.0	0.531	
1658.4			1654.4	0.182		1659.0	0.471	
1548.7			1615.9	0.210	FA			
1441.5	0.043	Acetone				1443.3	0.136	Acetone
1423.7	0.051	Acetone	1421.8	0.034	Acetone	1424.5	0.211	Acetone
			1392.1	0.054	Acetone	1374.9	0.274	Acetone
1368.3	0.105	Acetone	1371.5	0.085	Acetone	1355.5	0.206	Acetone
						1306.5	0.119	AA
1246.5	0.066	FA	1249.7	0.219	FA	1248.2	0.278	FA
1228.7	0.051	FA	1229.8	0.163	FA	1227.9	0.281	FA
1182.6	0.109		1184.1	0.099		1183.5	0.391	
1095.1	0.039	Acetone	1094.7	0.036	Acetone	1095.2	0.089	Acetone
			1078.2	0.046	Acetone			
			1016.2		AA	1019.9		AA
			970.9	0.078	FA	920.7	0.129	
804.9	0.621	FA	799.2	0.031	FA	758.9		
			721.3	0.082	FA	709.5	0.110	
554.2		Acetone	556.1		Acetone	554.9	0.138	Acetone

Table 7.9 Selected characteristic frequencies for the studied carbonyl compounds.

<u>Compound</u>	<u>$\nu(\text{cm}^{-1})$</u>	<u>Absorbance</u>	<u>Δ^1</u>
Acetone	1095	0.041	8.1
	1420	0.064	36.5
Acetaldehyde	1350	0.382	8.6
	888	0.042	20.4
	772	0.030	15.6
Acetic acid	1308	0.267	26.6
	1051	0.028	13.5
Formic acid	2585	0.078	83.6
	727	0.050	14.8
	799	0.072	31.6

¹ Full width at half height (cm^{-1}).

Whereas frequencies, bandwidths, and even relative intensities are expected to be reproducible for one compound in the standard mixtures provided the experimental procedure described is adhered to, some discrepancies regarding absolute intensities are bound to arise. This results from the assumption that all gas emanating from the deposition point is incident upon the cooled window. Probably this assumption is not correct; some of the gas will either be pumped away or will condense upon cooled parts of the apparatus other than the window. Because this situation will differ from cryostat to cryostat, it is essential to make sure that standard spectra are obtained using the same apparatus as is used to obtain spectra of the atmospheric samples. Standard and sample spectra should be collected under condition which mirror each other as closely as possible.

7.2.3.3 Diurnal variations

The peak heights for the $^{13}\text{CO}_2$ absorption at about 2280 cm^{-1} and the carbonyl group absorption at about 1720 cm^{-1} were measured for all the spectra of the samples

collected from Shinfield Road and the Chemistry Department car park. The peak height ratios of the carbonyl absorption to the $^{13}\text{CO}_2$ absorption were calculated (as listed in Tables 7.10 and 7.11) and plotted against the time of the day at which the samples were collected. This number is recorded as the X/ CO_2 ratio in Tables 7.10 and 7.11 and in the following text. The diurnal variations are shown in Figures 7.10 and 7.11 for Shinfield Road samples and the car park samples, respectively. The diurnal variations of Shinfield Road samples show different carbonyl concentrations in those samples collected between 8:00 and 9:00 a.m. The sample collected on the first day between 12:00 and 1:00 p.m. shows an increase in the carbonyl concentration while the samples collected at the same time of the other two days show a decrease in the carbonyl concentrations. This can be explained by referring to the IR spectra of these two samples. The IR spectrum of the sample collected between 12:00 and 1:00 p.m. on 20/3/1998 shows an absorption at 1700 cm^{-1} that gives an X/ CO_2 ratio of 0.364 in addition to that at 1720 cm^{-1} which was used in the diurnal variations. This is probably due to chemical reactions that take place with time and produce new carbonyl compounds with different absorption frequencies and different concentrations. The same behaviour is observed in the sample collected at the same time (between 12:00 and 1:00 p.m.) on 23/3/1998. A new carbonyl absorption is shown in the spectrum of this sample at 1711 cm^{-1} that gives an X/ CO_2 ratio of 1.211. The X/ CO_2 ratios of the samples collected between 12:00 and 1:00 p.m. in the second and the third days seem to decrease if only the absorptions at 1720 cm^{-1} are considered, but if the total X/ CO_2 ratios of both the absorptions at 1720 and 1710 cm^{-1} are considered they would be higher than those of the samples collected between 8:00 and 9:00 a.m. The third sample collected between 5:00 and 6:00 p.m. on 19/3/1998 shows almost the same X/ CO_2 ratio as the previous sample. The sample

Table 7.10 Variation of carbonyl frequencies and concentrations with time. (Shinfield Road Samples).

Time	X/CO_2 ratio ^a		
	19/3/1998	20/3/1998	23/3/1998
6:00	0	0	0
7:00			
8:00	0.192 (1725.3) ^b	0.766 (1726.1)	1.362 (1723.5)
9:00			
10:00			
11:00			
12:00	0.737 (1723.3)	0.267 (1720.2) 0.364 (1700.3)	0.796 (1726.0) 1.211 (1710.7)
13:00			
14:00			
15:00			
16:00			
17:00	0.749 (1724.9)	0.772 (1724.3)	1.176 (1725.7) 1.906 (1710.5)

^a X is the height of the carbonyl absorption, and CO_2 is the height of the $^{13}CO_2$ absorption at about 2280 cm^{-1} .

^b Values in parentheses indicate the frequencies (in cm^{-1}) of the carbonyl absorptions used to calculate the X/CO_2 ratios.

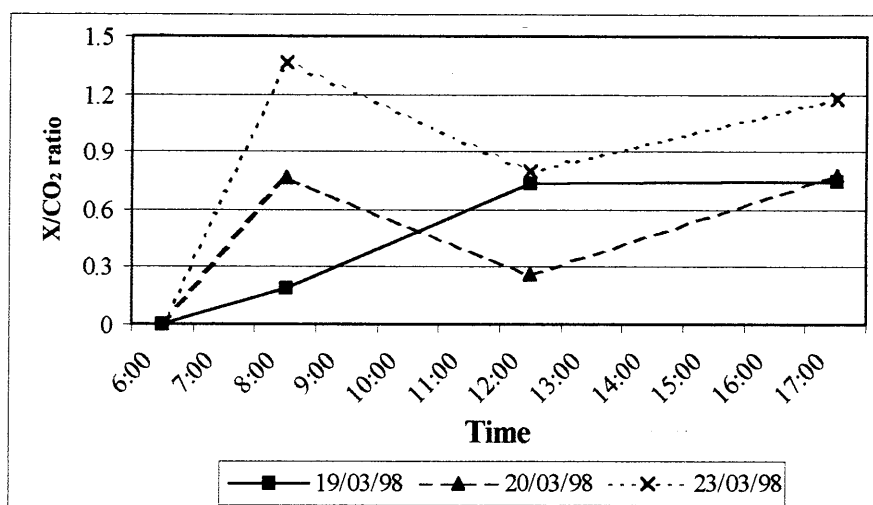


Figure 7.10 Diurnal variations of the carbonyl/ CO_2 ratios (Shinfield Road)

Table 7.11 Variation of carbonyl frequencies and concentrations with time. (Car park samples)

Time	X/CO_2 ratio ^a		
	24/3/1998	20/5/1998	21/5/1998
9:00	0.092 (1716.8) ^b	0.474 (1724.3)	0.491 (1723.5)
10:00			
11:00			
12:00	0.081 (1726.0)	0.074 (1705.8) 0.036 (1724.3)	0.733 (1726.6)
13:00			
14:00			
15:00			
16:00	0.072 (1701.9)	0.262 (1704.2)	1.095 (1723.6)

^a X is the height of the carbonyl absorption, and CO_2 is the height of the $^{13}CO_2$ absorption at about 2280 cm^{-1} .

^b Values in parentheses indicate the frequencies (in cm^{-1}) of the carbonyl absorptions used to calculate the X/CO_2 ratios.

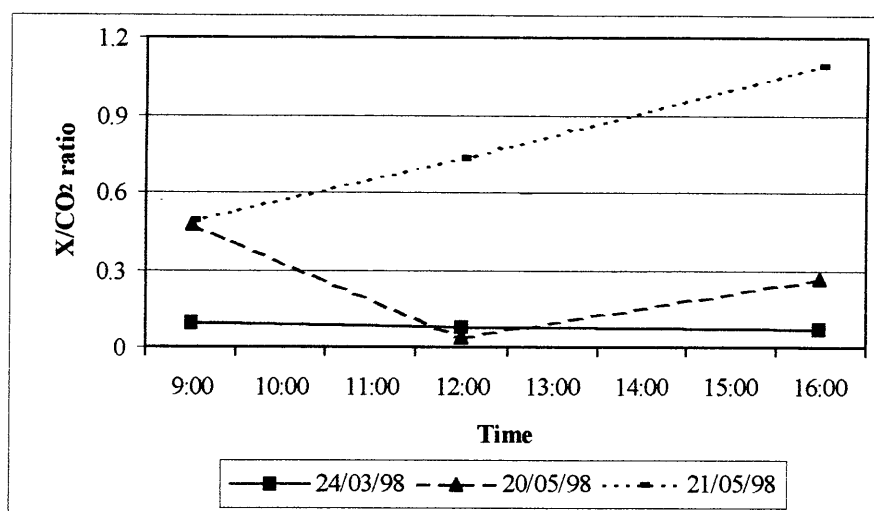
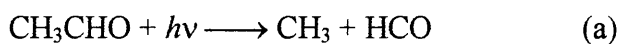


Figure 7.11 Diurnal variations of the carbonyl/ CO_2 ratios (The Chemistry Department car park).

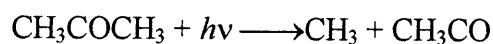
collected at the same time on the second day shows an increase in the ratio, and on the third day the sample collected at the same time also shows an increase in the ratio with the occurrence of a new absorption at 1710.5 cm^{-1} which gives an X/CO_2 ratio of 1.906. The samples collected in the morning probably contain aldehydes as the main carbonyl compounds as only the absorption at 1720 cm^{-1} is observed. The samples collected by mid-day and in the evenings probably contain aldehydes, ketones, carboxylic acids, or any combination of these compounds as both the absorptions at about 1720 and 1710 cm^{-1} are observed. This can be discussed in terms of chemical or photochemical reactions that take place.

Acetaldehyde has four theoretically possible sets of photo-decomposition products:



In the study of acetaldehyde photochemistry carried out in 1 atm of air,¹⁸ H_2 was not found in significant amounts, suggesting that (d) is unimportant. The two major paths were found to be (a) and (b). The majority of studies of aldehyde photolysis relevant to atmospheric conditions involve formaldehyde or acetaldehyde, since HCHO and, to a lesser extent, CH_3CHO are the aldehydes typically found in the highest concentrations in ambient air. Additionally, the radical formation rate from the photolysis of acetaldehyde is much less (approximately an order of magnitude) than from formaldehyde;¹⁹ this is expected to be true of the higher aldehydes as well which are present in even smaller concentrations.

Relatively few studies of simple ketone photolysis have been carried out under atmospheric conditions, although the vapour phase photooxidation of simple ketones in the presence of O₂ have been investigated in detail in classic studies in the laboratory of W. A. Noyes and coworkers.^{20,21} Thus acetone undergoes an α -cleavage reaction to form methyl and acetyl radicals:



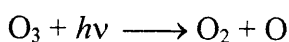
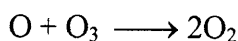
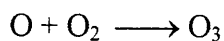
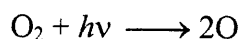
From the diurnal variation of the car park samples, it is shown that the samples collected on the first day (24/3/1998) contain low concentrations of carbonyl compounds. The concentrations decreased slightly with time. The frequency of the carbonyl absorption; however, is different in each sample. The spectrum of the first sample collected between 9:00 and 10:00 a.m. shows a carbonyl absorption at about 1717 cm⁻¹, while the spectra of the second and the third samples show carbonyl absorptions at 1726 and 1702 cm⁻¹, respectively. On the second day the sample collected between 9:00 and 10:00 a.m. shows an X/CO₂ ratio of 0.474 which corresponds to carbonyl absorption at 1724 cm⁻¹. This ratio decreased to 0.036 in the sample collected between 12:00 and 1:00 p.m. Another absorption occurs in the spectrum of the same sample at 1706 cm⁻¹ that gives a ratio of 0.074. The X/CO₂ ratio increased again in the sample collected between 4:00 and 5:00 p.m. and only the absorption at 1704 cm⁻¹ is observed. The sample collected on the third day showed only one absorption in the carbonyl position at about 1724 cm⁻¹. The X/CO₂ ratio of this absorption increased with time. The change in the carbonyl frequencies and concentrations in all the samples can be explained by the occurrence of chemical reactions as discussed earlier for Shinfield Road samples, i.e. that mainly (or only) aldehydes are present in the samples collected in the mornings and that levels of ketones and/or carboxylic acids build up later in the day.

Few carbonyl compounds were identified in the collected air samples as shown in Tables 7.3-7.9. Their distributions are characterised by a predominance of acetone and formic acid. The X/CO₂ ratios ranged from 0.074 in the car park of the Chemistry Department to 1.36 in Shinfield Road. The wide range of concentrations suggests that the concentration levels may be largely controlled by meteorological conditions and/or time of day. Motor exhaust is suggested as being one of the major sources of atmospheric organic acids and carbonyl compounds in general; however, this does not preclude the importance of the secondary production of organic acids or carbonyls in the atmosphere by photochemical reactions.

The study done by Kawamura *et al.*³ shows an identification of C₁-C₁₀ aliphatic organic acids and benzoic acid in air samples. Acetic acid was described to be the most abundant species followed by formic and propionic acids. Concentrations appear to decrease with an increase in chain length. Kawamura *et al.* have detected C₁-C₁₀ organic acids in motor exhausts as well. Their distribution is similar to that for air samples, except for a relatively high amount of benzoic acid. Acetic acid is predominant followed by formic and propionic acids. These acids are probably produced by incomplete combustion of gasoline. Their concentration in the exhaust is 43 ppb, which is 17 times higher than the average concentration of atmospheric organic acids. These results suggest that motor exhaust is an important source of organic acids in the atmosphere, in addition to possible photochemical production of organic acids from atmospheric organic compounds such as aldehydes.²²

7.2.4 Atmospheric Photochemistry

Because of the likely involvement of photochemical reactions, especially photo-oxidation reactions, in the formation of some of the carbonyl compounds and organic acids described in the preceding sections, it was considered relevant to include a brief overview of such atmospheric photochemistry here. In the stratosphere, a series of photochemical reactions involving O₃ and molecular O₂ occur. Ozone strongly absorbs solar radiation in the region from ~210 to 290 nm, whereas O₂ absorbs at ≤ 200 nm. The absorption of light, primarily by O₃, is a major factor causing the increase in temperature with altitude in the stratosphere. Excited O₂ and O₃ photodissociate, initiating a series of reactions in which O₃ is both formed and destroyed leading to a steady state concentration of O₃:



The steady state O₃ concentration in the stratosphere is essential for life on earth because it strongly absorbs light of $\lambda \leq 290$ nm. As a result, sunlight reaching the troposphere has wavelengths longer than ~290 nm. This short-wavelength cutoff sets limits on tropospheric photochemistry; thus only those molecules that absorb radiation >290 nm can undergo photodissociation. If there was a net destruction of O₃ in the stratosphere by chlorofluorocarbons and oxides of nitrogen, as has been proposed, increased radiation of $\lambda < 290$ nm would reach the earth's surface, leading to concomitant increases in skin cancer in humans as well as other effects on plants,

agriculture, and our climate. Of course tropospheric photochemistry would also be significantly affected.

In summary, the chemistry of the troposphere from pristine natural areas to heavily polluted urban areas is all part of one continuous cycle in which organics, oxides of nitrogen and sulfur, and inorganics such as O_3 play major roles. The highly reactive hydroxyl free radical (OH) drives the daytime chemistry involving those species. It is now recognised that at night the nitrate radical (NO_3) can play a major role in the chemistry of both remote and urban areas. Together, OH and NO_3 are central either directly or indirectly to such diverse phenomena as photochemical air pollution, acid rain and fogs, the fate of airborne toxic organics in the atmosphere, and the role of natural emissions in the chemistry of urban, rural, and pristine areas.²³

7.2.4.1 Photolysis Study

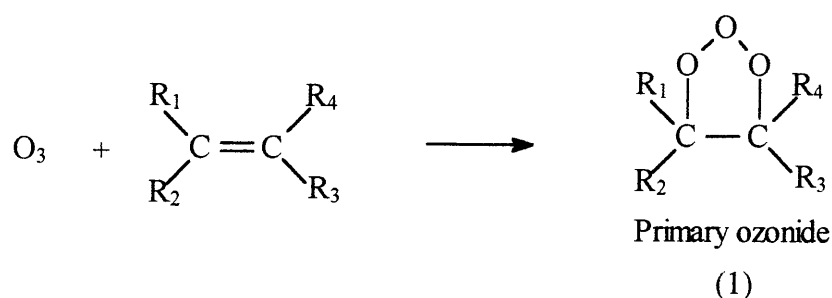
Formation of ozone in the urban atmosphere has been linked to the ambient concentrations of nitrogen oxides and of volatile organic compounds (VOCs). VOCs are produced from a variety of sources, including automotive engine emissions, localized manufacturing, and naturally occurring environmental processes. The C_2 - C_{10} hydrocarbon fractions, in particular, exhibit the greatest vapour pressures and play a critical role in the photochemical formation of ozone in the lower atmosphere.^{24,25} Reactions of $O(^1D)$ produced by UV photolysis of ozone have been studied by Taube *et al.*²⁶ for dilute mixtures containing O_3 and CS_2 or OCS , in xenon or argon at temperatures between 15 and 60 K, using IR spectrophotometry to identify products.

Over the years a number of methods have been used to study the intermediates in photochemical reactions. The technique of flash photolysis was introduced in 1949.²⁷

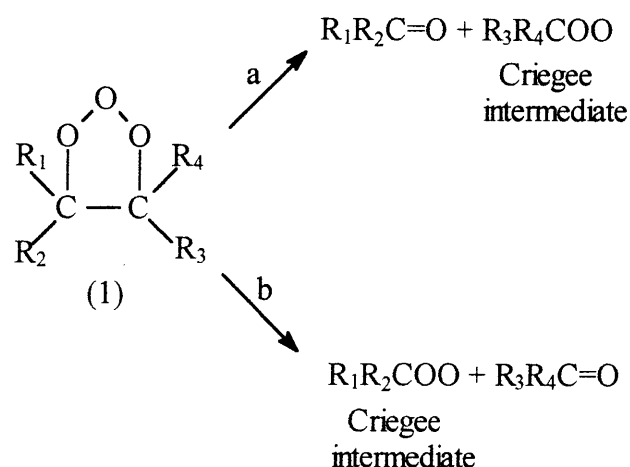
It is a powerful method of studying, as a function of time, transient species (mainly excited states and radicals) produced via electronic excitation of molecules by short pulses of UV or visible radiation. About a decade later pulse radiolysis, using the same principle, was applied to the study of similar species produced by pulses of high energy radiation.^{28,29} The study of photodissociation is greatly simplified if the secondary reactions which may follow can be prevented. Irradiation of the photosensitive substance dispersed at low temperatures in a transparent rigid matrix provides a simple means to this end. The rigid matrix impedes diffusion of primary products and the low temperature can reduce the rates of any secondary chemical reactions, (though not if they involve 'hot' primary photoproducts). Ideally it should be possible for the primary products to diffuse apart, but not together again. Transfer of their initial excess energy to the surrounding matrix allows some diffusion to occur, but as the heat is conducted away to the refrigerant, molecular diffusion rapidly ceases and any radical or molecular products are left isolated in the matrix. Unless it is allowed to soften and anneal, they may be stored for hours or longer, and their absorption spectra can be recorded at leisure when a sufficient concentration has accumulated.³⁰ With these thoughts in mind, and given the likely role of photo-oxidation reactions in the formation of some of the species described earlier in this thesis, it was decided to investigate the photo-oxidation of the simple hydrocarbon ethylene by ozone in CO₂ matrices. It was felt to be desirable to use a CO₂ matrix to study this reaction because the analytical work, reported elsewhere in this thesis, on carbonyl compounds (which are products of the ethylene-ozone reaction) has all been done using CO₂ matrices. It is of interest to note a recent study of the environmental effect on this reaction carried out by Haas *et al.*³¹ The reaction between ethylene and ozone was studied at low temperatures using argon and CO₂ matrices. The

products were identified by infrared spectroscopy. No reaction was observed in the argon matrix, while in solid CO₂ the reaction proceeded at temperatures as low as 25 K.

The gas phase reaction of O₃ with alkenes has been known for many years to produce aldehydes, ketones, and acids, as well as inorganics such as CO, CO₂, and H₂O. By analogy with the well studied reaction in the liquid phase, the gas phase mechanism³² is believed to involve an initial electrophilic addition of O₃ to the double bond to form a primary ozonide:



However, to date there is no direct experimental evidence for the existence of such primary ozonide in the gas phase. Subsequent cleavage of a peroxide O-O bond and the C-C bond in (1) leads to a carbonyl compound and a Criegee intermediate:



7.2.4.2 Sources of UV Light

Mercury discharge lamps are the most widely used sources of ultraviolet and visible radiation for conventional photochemical experiments. In this type of lamp a discharge is passed through mercury vapour and the electrically excited mercury atoms emit radiation. The relative intensity of the radiation at any wavelength is dependent upon the pressure of mercury inside the discharge tube (lamps operating at low pressure ($\sim 10^{-6}$ bar), medium pressure (~ 1 bar) and high pressure (~ 100 bar)). The disadvantage with high pressure lamps is that they operate at very high temperature so that water or forced air cooling the surrounding glass envelope is necessary. It can be seen that the emission occurs at specific wavelengths and that as the pressure inside the lamp is increased the emission occurs at a greater number of wavelengths.³³

7.2.4.3 Photolysis Procedure

In this study, photolysis was carried out using a 125-W high-pressure mercury lamp. Mixtures of ethylene in CO_2 and ozone in CO_2 were prepared separately to avoid any reaction in the gaseous phase and simultaneously deposited onto the cold window at 77 K. After deposition of the sample, an IR spectrum was recorded. The sample then was irradiated with the light from the high pressure mercury lamp focused on the CsI inner window which was rotated so that it is normal to the light beam. A shield made of aluminium foil was placed around the mercury lamp to avoid exposure to UV radiation during the experiment and a hole was made to let the light pass through. The cold cell was placed in front of the lamp keeping a distance of 80 cm between them. Because of the high temperature at which the high pressure lamps operate, it was necessary to blow

air to cool the surrounding glass envelope during the irradiation. An IR spectrum was recorded after photolysis.

In another set of experiments, mixtures of different amounts of ethylene, O₃ and CO₂ were prepared for photolysis study following the same procedure as in ethylene/CO₂ mixtures. The main line was evacuated after the addition of the compound to the external bulb (B₂) and filled with O₃ gas to a pressure greater than that in the external bulb to avoid the loss of any of the compound. The tap of the external bulb was then opened to allow mixing of the two gases. After the evacuation of the line, CO₂ gas was added and the three gases in the external bulb were mixed with the aid of the Teflon pieces previously added to the bulb. The bulb was connected to the cold cell and the mixture was deposited onto the cold window. IR spectra were recorded before and after irradiation.

7.2.4.4 Results of Photolysis

In the first experiment ethylene was photolysed in solid CO₂ at 77 K in the presence of ozone. The IR spectrum of ethylene isolated in a CO₂ matrix is discussed in detail in Section 2.5.7. The IR spectrum given in Figure 7.12 is of a mixture of ethylene and ozone in a CO₂ matrix before irradiation. By comparing the frequencies in this spectrum to those of the CO₂ matrix-isolated ethylene (Figure 4.18) many differences are observed. The most obvious difference is the presence of a new absorption at 1724 cm⁻¹ which can be assigned to a C=O stretching vibration. This observation suggests that a reaction between ethylene and ozone has already started before the mixture is irradiated forming a carbonyl bond. The in-plane and out-of-plane C-H bending vibrations of ethylene occur at 1437 and 947 cm⁻¹, respectively, show no significant

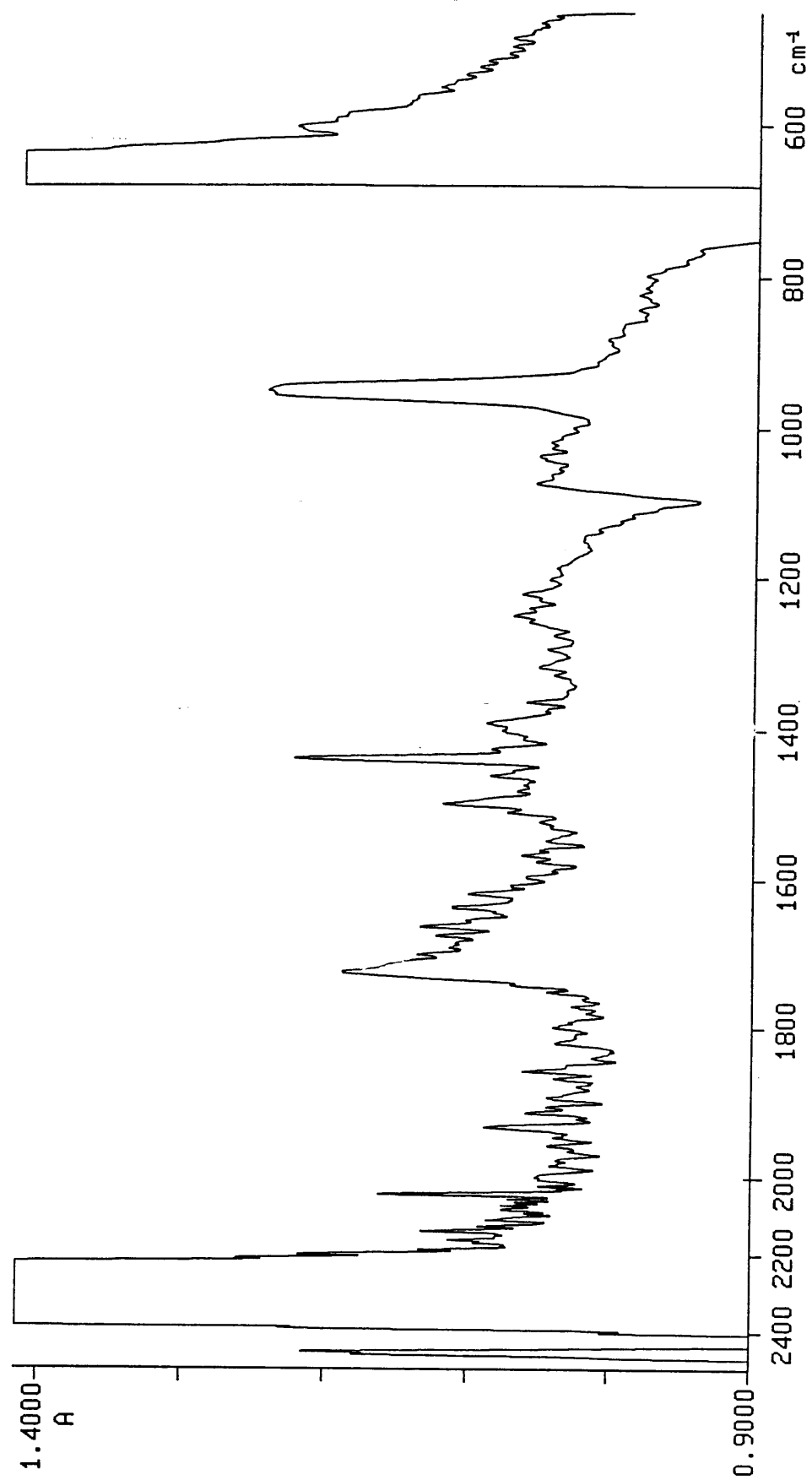
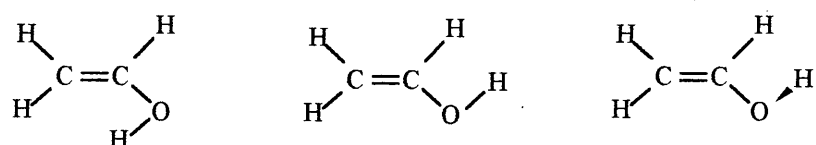


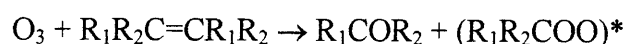
Figure 7.12 IR spectrum of ethylene/ozone/ CO_2 mixture before irradiation.

shifts from the ethylene in CO₂ matrix position and demonstrate, however, that a considerable amount of unreacted ethylene is present in the matrix.

The reaction of ozone with olefins has considerable practical importance in organic chemistry and in photochemical smog problems. In previous studies³⁴ of the reaction between oxygen atoms and solid ethene, acetaldehyde and ethylene oxide were identified as the sole addition products. A third possible "addition" product of the O atom-ethene reaction is vinyl alcohol, CH₂=CHOH:



Major uncertainties include the nature and yields of the carbonyl products and the subsequent reactions of the biradicals. Grosjean *et al*³⁵ have identified carbonyl products and have measured their yields in experiments involving the gas phase reaction of ozone with symmetrical alkenes including ethylene. Formation yields (carbonyl formed/ozone reacted) of primary carbonyl were close to the value of 1.0 that is consistent with the simple reaction mechanism:



In Figure 7.13 is shown the spectrum of the same ethylene/ozone/CO₂ mixture after being irradiated for 10 minutes. The intensities of most of the absorptions of ethylene have decreased suggesting a further reaction upon irradiation. Very interestingly the band at 1724 cm⁻¹ which is assigned to a ν(C=O) vibration has decreased in intensity in this spectrum. It has given way to a broadish feature probably due, at least in part, to an impurity of ice. Although it is difficult to identify any specific features in this region of the spectrum with certainty there do appear to be features at

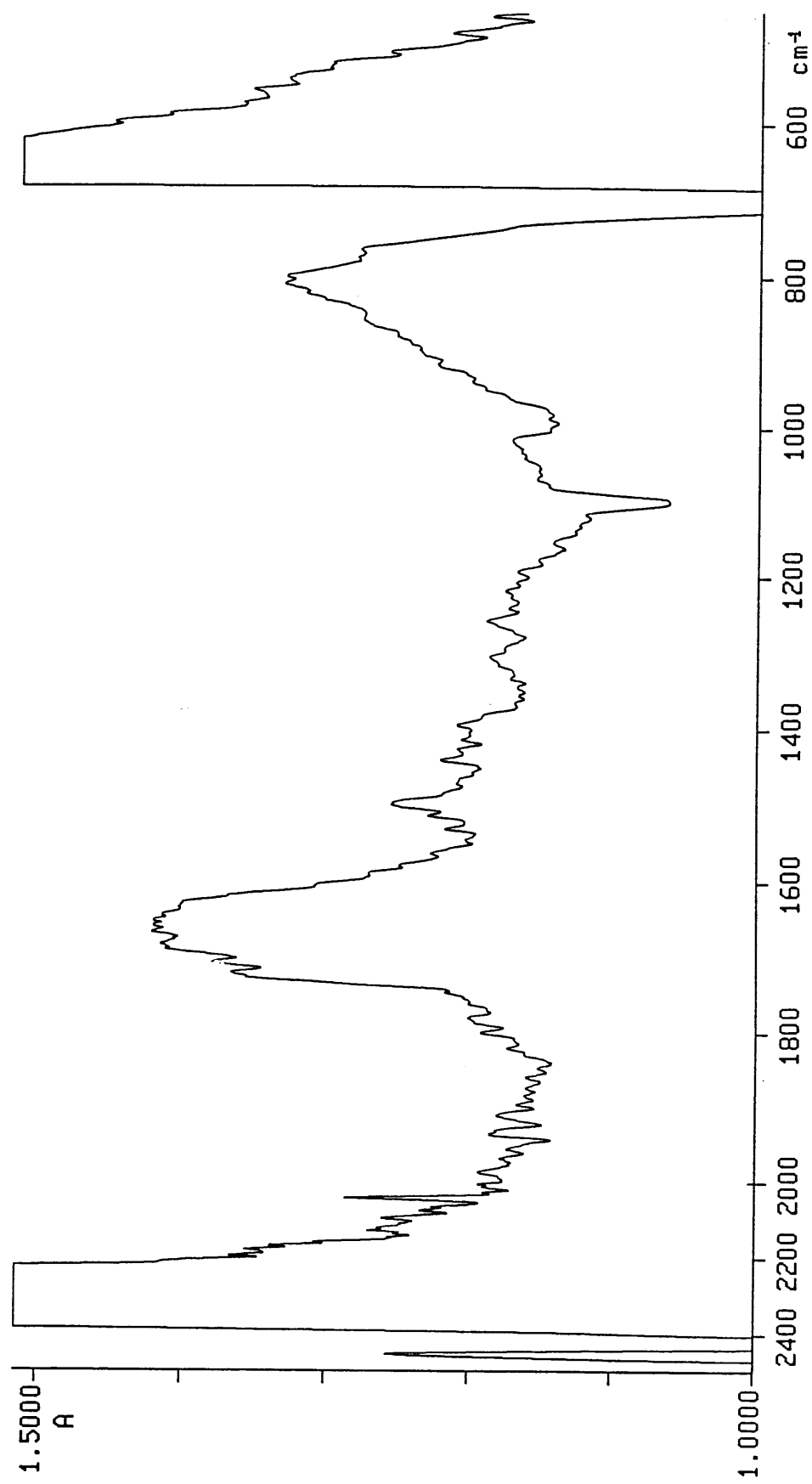


Figure 7.13 IR spectrum of ethylene/ozone/CO₂ mixture after 10 minutes irradiation.

1719, 1706, 1681 and 1665 cm^{-1} . The most likely course for the reaction is therefore that ethylene and ozone react upon mixing to give a carbonyl compound which absorbs at 1724 cm^{-1} and is therefore likely to be acetaldehyde.³⁶ Upon irradiation this compound gives way to ones which absorb at 1706, 1681 and 1665 cm^{-1} . The first band probably arises from acetone.³⁷ The last two bands could conceivably be assigned to matrix-isolated water.³⁸

These photochemical reactions in CO_2 matrices therefore provide something of model for the atmospheric chemistry previously reported. First ethylene and ozone react to yield acetaldehyde which generates acetone upon photolysis. This is the same pattern as was seen for the samples collected on Shinfield Road and in the Chemistry Department car park where high levels of ketones were only seen later in the day when photochemical reactions had occurred.

In the second experiment, where a premixed sample of ethylene, ozone and CO_2 was deposited, bands due to acetaldehyde and acetone were seen. This suggests that acetone may also be formed by a secondary, non-photochemical reaction when the reagents are allowed to react in the gas phase prior to deposition.

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Summary

The matrix isolation technique has been investigated in this study and applied to the isolation of some carbonyl compounds in carbon dioxide matrices. As spectra of the studied compounds have never previously been recorded in CO₂ matrices, these spectra have been analysed in some detail and compared with spectra obtained for the same compounds in more conventional matrices and with gas phase spectra. Frequency shifts in most of the absorptions have been observed and explained by matrix effects, i.e., the interactions between the trapped molecule and the surrounding matrix, the presence of more than one trapping site in the matrix, and the site symmetry of the trapped species which may cause splitting of any degenerate vibrations.

To construct calibration curves, a suitable spectral line was chosen for each compound studied. The C=O stretching vibrations at about 1717 cm⁻¹ and 1722 cm⁻¹ were selected for acetone and acetaldehyde, respectively. The double peak at about 1262 and 1227 cm⁻¹ assigned to the C-O stretch was chosen for formic acid. The C-O stretch at about 1307 cm⁻¹ was selected for acetic acid. The band at about 2247 cm⁻¹ was chosen for N₂O. The band around 1333 cm⁻¹ was selected for SO₂, and the CH₂ bending vibration around 945 cm⁻¹ was chosen as the suitable feature for ethylene. An infrared absorption band of CO₂ was used as an internal calibrant and all the absorbance measurements were made as a ratio of the absorbance of the selected band of species X to the absorbance of a band of CO₂. The selected absorption of CO₂ used was a band of weak intensity centered at about 2282 cm⁻¹ which arises from the asymmetric stretch of the isotopomer ¹⁶O¹³C¹⁶O present in natural abundance. The calibration curves were constructed by plotting the peak area ratio of the selected absorption of the compound to that of CO₂ against the concentration of the compound in CO₂ matrix. All of the

calibration curves are linear with different detection limits. N₂O shows the best detection limit of all the studied compounds which is 0.01% in CO₂ or 32.5 ppb in air. Acetone, acetaldehyde, acetic acid and ethylene were measured to a level of 1% in CO₂ or 3.3 ppm in air. Formic acid was detected to a limit of 0.7% in CO₂ or 2.3 ppm in air, while SO₂ has a detection limit of 0.1% in CO₂ which is equivalent to 325 ppb in air.

IR spectra of some deuterated carbonyl compounds in CO₂ matrices were analysed to study the effect of the CO₂ matrix on the IR spectra. The spectra of the deuterated compounds were compared to those of the non-labelled compounds. The carbonyl absorption in the CO₂ matrix-isolated acetone-*d*₆ occurs as a strong band at 1701 cm⁻¹ (which is close to the value of acetone-*d*₆ in CCl₄ solution) and a weak band at 1734 cm⁻¹ (which is close to the argon matrix value). A dipole-dipole interaction between the CO₂ matrix and the acetone molecules is probably the reason for this observation. The carbonyl absorption which occurs at 1715 cm⁻¹ in CO₂ matrix-isolated acetic acid is observed as double peaks at 1705.5 and 1727 cm⁻¹ in acetic acid-*d* and at 1712 and 1729.5 cm⁻¹ in acetic-*d*₃ acid-*d*. This may suggest the presence of deuterated acetic acid molecules with or without dipole-dipole interaction to the host CO₂ molecules. The C=O stretching frequency shifted from 1712 cm⁻¹ in the CO₂ matrix-isolated formic acid to 1700 cm⁻¹ in the CO₂ matrix-isolated formic-*d* and-*d*. The O-D stretching band is observed at 2606 cm⁻¹ with a large shift from the position of the O-H stretching vibration. The largest shift is observed in the C-D stretching frequency which occurs as a doublet at 2098 and 2035 cm⁻¹ for DCOOD comparing to the C-H stretching vibration of HCOOH which occurs at 2958 cm⁻¹.

One of the objectives of this study was to use the matrix-isolation technique in the analysis of atmospheric pollutants (principally carbonyl compounds). Since a portable vacuum line fitted with a spiral trap which could be cooled to liquid nitrogen

temperature did not give encouraging results in fractionating the atmospheric compounds, adsorbent tubes were used to preconcentrate the atmospheric carbonyl compounds. Activated carbon was selected as the adsorbent material of choice as it gave the best recoveries among four studied adsorbent materials. The prepared gas mixtures or “real” air samples are adsorbed onto the activated carbon then thermally desorbed while depositing onto the cold window at 77 K. The method is simple, fast and gives reasonable results.

The main effort of the work described in this thesis has been devoted to establishing a spectrophotometric technique which improves upon conventional infrared methods by combining the intrinsic advantages of both Fourier transform infrared (FTIR) spectroscopy and matrix isolation (MI). With a simple apparatus using carbon adsorbent tubes, air samples can be collected and analysed for the presence of carbonyl compounds using FTIR-MI technique. Air samples from Shinfield Road and the Chemistry Department car park have been collected and analysed and their IR spectra shown sharp and well-resolved lines that have been assigned according to the spectra of the standard studied carbonyl compounds. Carbonyl absorptions have been observed in the spectra of all the samples at about 1710, 1720 or 1725 cm^{-1} . Spectral differences observed between the samples collected at different times of the day have been discussed in terms of possible photochemical reactions that take place with time. Some of these photochemical reactions have been modelled also using CO_2 matrices. The range of application of this technique can be extended to other organic compounds of higher molecular weight. It is clear that the sensitivity of the method can, in principle, be improved to be used for quantitative analysis.