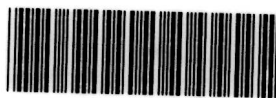# MATRIX ISOLATION

A technique for the study of reactive
inorganic species

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MATRIX ISOLATION

Preface

Matrix isolation is a technique developed over the last two decades which enables reactive, short-lived molecules to be trapped in a solid matrix and studied spectroscopically. This book aims to show how this may be done in practice. It assumes that the reader is familiar with much basic physics, chemistry and spectroscopy, but the nature and formation of the matrix and details of its interactions with trapped species are covered explicitly. There are also chapters on various technical matters relevant to the production and study of matrix-isolated samples.

A major portion of the book consists of specific examples where study of matrix-isolated samples has contributed to our understanding of the nature of small, reactive molecules. As well as 'free radicals' and the like we have included what may be termed 'high temperature monomers', species such as sodium chloride that are normally met only in a polymeric form. The monomeric molecules can be studied in matrices and information concerning bonding and structure obtained. We have attempted to maintain a critical stance in discussing the examples, so as to bring out clearly the physical and chemical significance of the results, as well as to indicate where the interpretation of the results is less than certain.

In the examples we have interpreted the term 'inorganic' rather widely, including a number of small carbon-centred species, as it seemed pointless to exclude derivatives of one element arbitrarily. On the other hand we have barely touched on the vast field of study of organic (and more recently 'hetero-organic') radicals in organic glassy matrices.

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1   Introduction

The chemist is usually concerned to know the structure and other properties of individual molecules, yet matter is rarely found in the form of isolated molecules. Intermolecular interactions dominate the physical nature of matter in the solid and liquid phases, and are experimentally observable even in gases, where they are smallest. In general the 'molecular' properties of a substance can only be deduced from gas-phase studies. The intermolecular interactions are strongest between chemically reactive species such as most atoms, free radicals and 'high temperature monomers', all of which can be studied in the gas phase only at low concentrations and high effective temperatures. Even under such extreme conditions some species are so reactive that they exist for only a few micro- or milliseconds after they are formed, so that the study of their molecular properties is a difficult matter.

The technique of matrix isolation is one result of attempts to overcome some of the difficulties associated with the study of very reactive molecules. In essence, the method involves the trapping of the molecule in a *rigid cage* of a *chemically inert* substance (the *matrix*) at a *low temperature*. The rigidity of the cage prevents diffusion of reactive molecules, which would lead to reaction with other such species. The inertness of the matrix material prevents loss of reactive molecules by reaction with their environment. The low temperature, besides contributing to the rigidity of the cage, serves to reduce the rate of possible internal rearrangements that require any activation energy. Under such conditions molecules that normally have very short lifetimes can be preserved indefinitely and studied at leisure.

In practice, few materials other than the rare gases and molecular nitrogen are chemically inert enough to serve as matrices for the most reactive species. The formation of a rigid matrix implies the use of temperatures not exceeding about one-third of the melting point of the solid, i.e. temperatures of 9 K for neon, 29 K for argon, 40 K for krypton, 55 K for xenon or 26 K for nitrogen. As the lowest tempera-

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ture attainable using liquid nitrogen as coolant is 63 K, the triple point of nitrogen, the most inert materials available can only be used as matrices if colder refrigerants are employed. Only liquid hydrogen and liquid helium are suitable; they are usable over the ranges 12–33 K and 2–5 K under 'boil off' pressures that can be controlled to adjust the temperature of the liquid. The necessity for the use of such low temperatures has controlled the development of the technique of matrix isolation.

The first experiments recognisably related to our subject were in fact carried out in 1924 in the pioneering cryogenic (low temperature) research laboratory of Kamerlingh Onnes in Leiden. Vegard studied the emission spectra of oxygen and nitrogen atoms produced by electron, proton or X-ray bombardment of impure solid nitrogen or solid mixtures of nitrogen and rare gases, using liquid hydrogen and liquid helium as refrigerants. These were not available elsewhere at that time, and the experiments were not repeated and extended until about thirty years later. In the early 1950s Broida in Washington and Pimentel in Berkeley began to use the matrix isolation technique in the study of atoms and reactive molecules, but the method spread only slowly until the wider availability of liquid helium in the early 1960s and the advent of microrefrigerators in the last few years made it possible for matrix isolation experiments to be performed outside the United States or the immediate neighbourhood of physics departments with surplus liquid helium. The experimental procedure has become so convenient and cheap that argon or nitrogen matrices at 4 K are increasingly used in the study of stable molecules although the low temperature and complete chemical inertness are strictly unnecessary.

The matrix isolation technique necessarily involves a combination of several distinct technologies, each of which interacts with the others. The most basic factor, the low temperature needed to give rigid matrices, implies cryogenic technology, and in turn requires the use of high vacuum techniques without which low temperatures cannot conveniently be maintained. The nature of the matrix, the low temperature and the need to isolate the sample in a vacuum all imply that only spectroscopic methods can be used to study matrix-isolated species, and the experimental technique is to a large extent dominated by the need to expose the sample to the spectrometer at the same time as cooling it in a high vacuum.

The main spectroscopic methods used to study matrix-isolated species are electronic absorption and emission spectroscopy in the

visible and ultraviolet regions, vibrational absorption spectroscopy in the infrared and electron spin resonance (e.s.r.) spectroscopy. Electronic and vibrational absorption studies are usually carried out on samples deposited on cooled windows transparent to the radiation concerned (fig. 1.1(*a*)). Electronic emission spectroscopy, which involves excitation by an intense source of radiation while the spectrometer 'views' the excited sample, is better carried out with the sample deposited on a metal surface (fig. 1.1(*b*)). This type of sample arrangement is also suitable for Raman spectroscopy.

E.s.r. spectroscopy, where the sample is contained in a 'resonant cavity' in a strong magnetic field and irradiated with radiofrequency waves, is often carried out with the sample deposited on a synthetic sapphire rod or plate (fig. 1.1(*c*)). In each case heat transfer from the window, metal surface or rod to the coolant reservoir must be as efficient as possible. This is usually ensured by the use of copper or brass connecting parts which must be as short as possible. The sample sample holder and coolant reservoir must be contained in a vacuum vessel, so windows are provided for ingoing and outgoing radiation. There must also be provision for introducing the matrix gas and sample.

The matrix-isolated species is of course not completely free of intermolecular interactions. The magnitude of these is, however, much lower in solid rare gases or nitrogen than in more normal solid or liquid systems, and it is usually possible to regard the effect of the matrix as a perturbation of the molecular property required. The observed spectroscopic properties may then be taken as representative of those of the free molecule.

The arrangement of this book follows the order suggested in the paragraphs above. The properties of matrix materials are dealt with in chapter 2, chapter 3 covers some relevant aspects of low temperature, high vacuum and oven technology, while the methods by which matrix-isolated reactive species may be prepared are described in chapter 4. The spectroscopic methods used in the study of matrix-isolated substances and the effects of the matrix on the observed spectroscopic properties are discussed in chapters 5 and 6 respectively. Two chapters of examples of systems studied by matrix isolation serve to illustrate the wide scope of the method, and we end with a brief attempt to sum up the achievements of matrix isolation to date and to indicate its further potential.
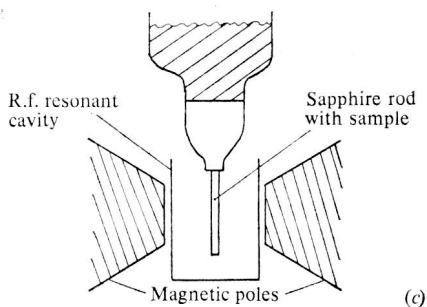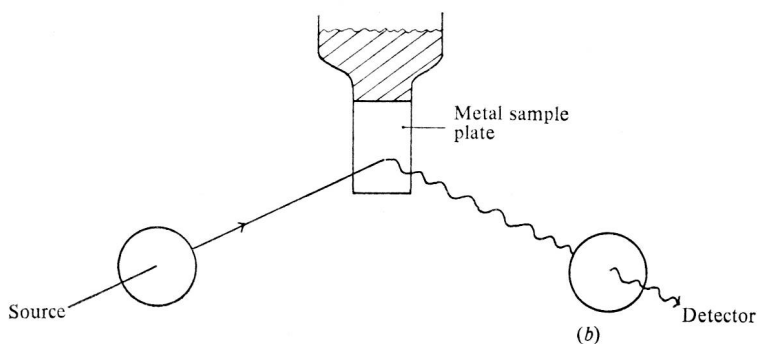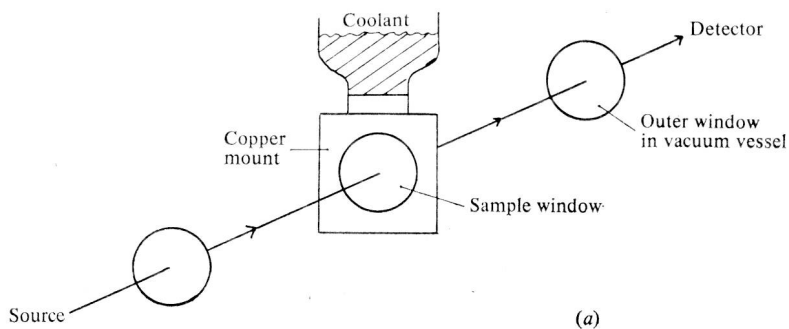
Fig. 1.1. Typical experimental arrangements for spectroscopic studies of matrix-isolated samples. (*a*) Absorption experiment, (*b*) emission experiment, (*c*) e.s.r. experiment.

2 Matrix materials and their properties

As we noted in chapter 1, most matrix isolation of reactive species is done using solid rare gases or nitrogen as matrix material because of the high degree of chemical inertness of these materials. They are also almost uniquely free of absorption spectra that would interfere with spectroscopic detection of the isolated species. Argon and nitrogen are readily and cheaply available, being obtained in large quantities by the fractional distillation of liquid air. The other rare gases are more expensive, being present in the atmosphere only in very small amounts. Only helium is found in relatively concentrated form, in some natural gas samples, from which it is extracted on a large scale in the United States.

There are, however, other potential matrix forming materials, and before going on to discuss the structures and properties of matrices in general we shall briefly list some of the disadvantages of these alternatives.

2.1 Other potential matrix materials

Helium and hydrogen. These may be considered together because, despite their obvious suitability on the grounds of lack of interfering spectra and chemical inertness in all or most likely circumstances, they are quite unusable because they do not form rigid solids and have high vapour pressures even at 4 K. Helium does not solidify at all at pressures less than 25 atmospheres, and hydrogen melts near 14 K. The very low boiling points and high vapour pressures make it impossible to maintain high vacuum conditions in the presence of the condensed phases. This in turn makes it very difficult to maintain low temperatures without elaborate insulation, because, as we shall discuss in chapter 3, heat is transferred across a gas-filled space much faster than across an evacuated space. We include some of the properties of helium and hydrogen in table 2.2 for comparison.

Oxygen, fluorine, chlorine. Although these substances have no inter-
fering absorption bands in the infrared spectrum they are not much
used because of their high chemical reactivity. A few experiments
using oxygen as matrix material have been reported. In most of these
the chemical reactivity was used to advantage, for when an atomic
product of photolysis, discharge or evaporation reacts with matrix
material to form MO_2 this is more readily detected and identified
than the original atom.

Carbon monoxide. Although this material has a strong infrared
absorption it has been much used as a matrix material. Its chemical
reactivity is not much greater than that of nitrogen, with which it is
isoelectronic. The chemical reactivity is often used to good effect;
a large number of new metal carbonyl species have been detected
when metal atoms are condensed with a carbon monoxide matrix
(see chapter 8). The physical properties of carbon monoxide are
similar to those of argon and nitrogen.

Methane and other alkanes. Again, although these substances have
infrared absorptions they are sometimes used as matrix materials.
Their chemical reactivity is low because of the high bond strength of
the C–H and C–C bonds and their low polarity. Branched alkanes of
C_5 to C_8 size are particularly widely used in the rather distinct
technique of organic matrix isolation, as they give rigid glassy solids
at 77 K (liquid nitrogen temperature). These glasses can be handled by
more conventional techniques than are needed for rare gas matrices;
their use is further discussed at the end of chapter 4. Methane is
sometimes used in the same way as the rare gases and nitrogen, and
is included in table 2.2.

CO_2, SF_6 and CCl_4. Despite the even higher degrees of chemical
reactivity and spectral interference to be expected from these larger
molecules, they are used to some extent. They are particularly useful
at rather higher temperatures than those necessary for the more inert
matrix materials.

2.2   The structures of matrices

It is now pertinent to consider what the actual structure of the matrix,
at the atomic or molecular level, may be. Three possibilities may be
clearly defined, which we shall term the *single crystal*, the *glassy* and
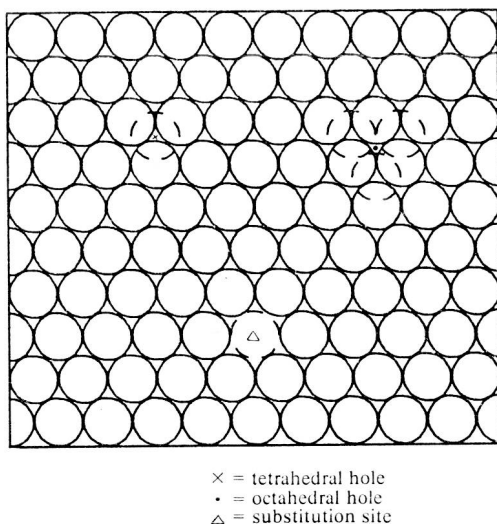the *microcrystalline* models respectively.

× = tetrahedral hole
• = octahedral hole
△ = substitution site

Fig. 2.1. Single crystal model.

Single crystal model. This has great advantages as a model, as the stable crystal structures of the matrix forming materials at low temperatures are well known, having been investigated by X-ray diffraction methods. In addition, the relative simplicity of this model, in which interstitial and substitutional sites are clearly defined (see fig. 2.1) makes it a favourite starting point for analysis of possible sites for matrix-isolated atoms and molecules.

Unfortunately, it is highly unlikely that a comparatively large volume of solid can be deposited in the form of a single crystal under the conditions used. These involve:

(i) a large-area condensation surface, so that many initial growth points must be expected;

(ii) fast freezing of a gas at a pressure and temperature considerably higher than the triple point to a solid at a temperature well below the triple point, so that the equilibrium is 'rushed through', and

(iii) the formation of the solid at such a temperature that diffusion of matrix atoms cannot occur in the bulk solid, preventing crystallisation after deposition.

Glassy model. In this case a random arrangement of matrix atoms is postulated (fig. 2.2); the density of the solid will be less than that of the perfect crystal, which is usually close-packed. The number of
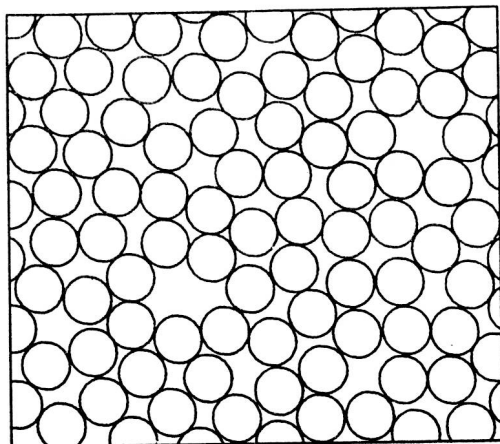
Fig. 2.2. Glassy model.

near neighbours for each atom will also vary randomly and will on average be less than 12, the number for a close-packed structure. As a result even 'single substitutional' sites, in which an isolated species replaces a single matrix atom, will vary in size and coordination, while the distinction between interstitial and substitutional sites will be to some extent lost.

The matrix-isolated species would then be expected to behave as if it were in an infinitely viscous liquid solution, and the effect of the matrix should be to broaden spectral bands. As we shall see later this is by no means commonly observed, and indeed one of the greatest advantages of the matrix isolation method is that spectral bands are usually extremely sharp, especially in the infrared and Raman. We must therefore reject the glassy model as appearing to predict broad bands where sharp bands are usually observed.

Microcrystalline model. The most plausible model is that of the microcrystalline solid. Here small regions of ordered structure exist, in which clearly-defined sites may be expected, but their crystal axes are not correlated and regions of random structure are required in between crystalline parts (fig. 2.3). These may be regarded as grain boundaries, so long as it is remembered that the crystalline regions may be so small that the 'crystalline' and 'boundary' regions take up comparable proportions of the solid.
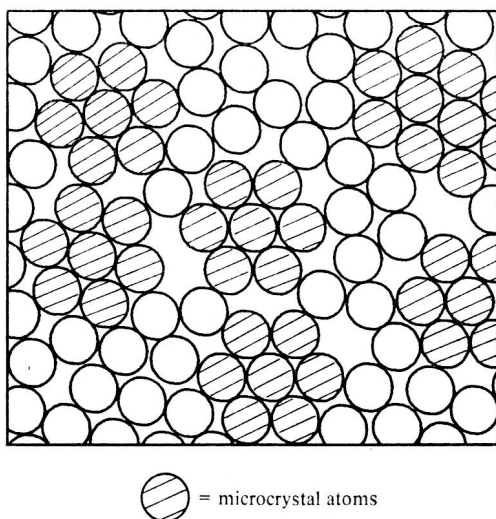
= microcrystal atoms

Fig. 2.3. Microcrystalline model.

At equilibrium it would be expected that any impurities (e.g. matrix-isolated species) would be segregated at the grain boundaries, but in the absence of diffusion this segregation cannot occur. When diffusion is allowed to occur it is certainly common for the sharp spectra characteristic of matrix-isolated species to be replaced gradually by broader bands more like those produced by substances in liquid solution.

This model is, however, very hard to treat quantitatively. We may not necessarily assume, for instance, that all crystalline regions adopt the structure that is most stable at the temperature of the experiment. In the absence of diffusion it is perfectly possible for two different crystalline phases to coexist, especially if they are physically separated by random regions. The range of possible sites in and between the crystalline and random regions is large, and it is extremely difficult to deal with the effects of long-range interactions between matrix-isolated species.

It is usual, therefore, for analysis of matrix spectra to begin by assuming that the single crystal model is appropriate. Other solid structures may then be considered if necessary as perturbations. We must thus discuss the *crystal* structures of typical matrix materials.

2.3   Crystal structures of matrix materials

The most commonly used matrix materials, the rare gases neon, argon, krypton and xenon, crystallise in the face-centred cubic structure (cubic close-packed). Each atom is surrounded by 12 equidistant nearest neighbours, and the symmetry of the site is that of the octahedron, O_h. This structure is the stable form for the solids at any temperature below the melting point.

There is, however, a less stable structure. This is simply the other close-packed structure, hexagonal close-packed. Again there are 12 nearest neighbours, but the symmetry of the site is lowered to D_{3h}. While this structure is less stable thermodynamically it is by no means certain that microcrystals with this structure may not form during deposition from the gas phase. Diffusion in the solid would lead to transformation to the more stable form, but is not always possible if the solid is rapidly cooled.

It has been shown that incorporation of even small amounts of nitrogen or oxygen into solid argon can render the hexagonal close-packed phase stable near the melting point, while a solid containing 40 % argon and 60 % nitrogen is stable with the hexagonal structure at all temperatures down to absolute zero. It is therefore rather important that the apparatus should be free from leaks during deposition of the matrix to prevent contamination of the solid with air, which would tend to alter the crystal structure.

It is apparent that other impurities, such as matrix-isolated species, in the matrix could have similar effects, at least locally. This could result in some microcrystalline regions having a hexagonal structure while others had a cubic structure. While X-ray diffraction can give information on the structure of a bulk solid it is not usually sensitive enough to detect small disturbances in structure in localised regions that may comprise less than 1 % of the total bulk.

Nitrogen, another important matrix material, has two stable solid phases, which transform reversibly into each other at 35.6 K in the presence of gaseous nitrogen. In the high temperature form (β-N_2) some degree of rotation of the molecules of nitrogen is possible, and they behave as near-spherical bodies in a hexagonal close-packed arrangement. Below 35.6 K, in the α-form, this rotation is 'frozen out' and a structure appropriate to cylindrical molecules is adopted. This is derived from the cubic close-packed structure. This is the only structure strictly relevant to matrix isolation, as solid nitrogen is rigid only below 20 K. However, the rearrangement involved in the