

Matrix Isolation

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1. WHAT IS MATRIX ISOLATION?

If one peruses the literature on reactive intermediates, or discusses the subject with colleagues interested in that field, one soon finds that the term “matrix isolation” means different things to different people, so some semantic clarification appears to be in order at the outset.

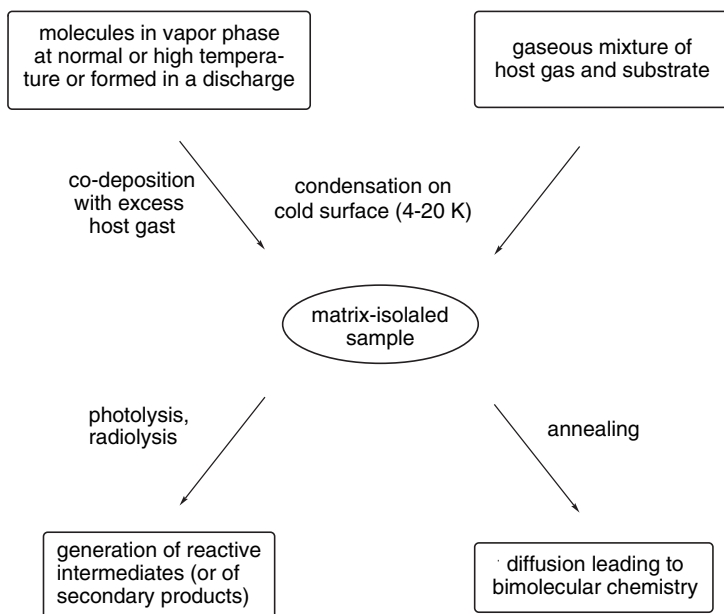
The term “matrix isolation” was coined by George Pimentel who pioneered this field^{1,2} together with George Porter.³ Pimentel intended this term to refer to a method whereby a substrate is mixed with a large excess of an (usually unreactive) host gas and is condensed on a surface that is sufficiently cold to assure rapid solidification of the material. In this way, one ends up with a sample where (ideally) each substrate molecule is immobilized in a cavity surrounded by one or more layers of inert material and is thus “isolated” from the other substrate molecules in a “matrix” of the host gas.

In the course of time, the term matrix isolation came to be applied in a more general sense, encompassing a range of techniques where guest molecules are trapped in rigid host materials and are thereby prevented from undergoing diffusion. Such host materials may be, for example, crystals, zeolites or clays, polymers, boric acid glasses, or cryptands. However, most relevant in the present context are studies of reactive intermediates in *frozen solutions* that are often referred to under the heading of “matrix isolation,” but should perhaps more appropriately be referred to as “low-temperature spectroscopy in rigid media.”

Such experiments have provided (and continue to provide) much valuable spectroscopic information on many types of reactive intermediates discussed in this volume. In particular, solvents that provide transparent glasses on freezing, such as the ether–pentane–alcohol (EPA) mixture introduced by G.N. Lewis,⁴ methyltetrahydrofuran (MTHF), or the mixture of CFCl_3 and $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ discovered by Sandorfy⁵ have proven to be very convenient media for obtaining ultraviolet–visible (UV–vis) absorption spectra of reactive intermediates that can be generated by photolysis or radiolysis at 77 K. On the other hand, many odd electron species (radicals, triplet biradicals and carbenes, radical ions) were characterized by electron spin resonance (ESR) methods in solvents that form polycrystalline matrices long before matrix isolation techniques became widely available.

However, to include this enormous body of work, and the techniques that stand behind it, into the present chapter would surpass its limits. Hence, the reader is encouraged to visit the contributions on carbocations, carbanions, radicals, radical ions, carbenes, silylenes, nitrenes, and arynes where studies involving frozen solutions will be referred to in their topical context. Thus, this chapter will deal only

with matrix isolation in the “proper” sense of the word, which can be summed up in a sketch (Scheme 17.1, adapted from the book of Almond and Downs⁶) that encompasses in schematic form most of what will be discussed in the following sections.



Scheme 17.1

2. WHY MATRIX ISOLATION?

When one wants to engage in the study of species that are only of fleeting existence under ambient conditions, one has basically two choices: either one looks at them very quickly, that is, immediately after their formation, which nowadays can be as short as a few femtoseconds, or one attempts to form or trap them under circumstances where they can be studied leisurely, using conventional spectroscopic tools. The two methods are complementary in that time-resolved techniques provide *kinetic information*, but often at the expense of spectroscopic detail, whereas investigations under “stable conditions” can yield much more detailed insight into the *electronic and* (often indirectly) the *molecular structure* of reactive intermediates.

Note that there is a price to pay for this, that is, the transfer of these species from their “natural” environment, where they occur as fleeting intermediates on the way from reactants to products (e.g., aqueous solution or the protein environment of an enzyme in the case of intermediates of biological processes), to an “artificial” environment. This transfer may impart different properties onto reactive intermediates and their chemistry, a feature that should be remembered when one uses insight

gained from studies of chemically isolated species to draw conclusions about their behavior in their “native” environment.

With the above caveat in mind, one usually tries to create an environment that provides for minimal interaction with the target reactive intermediate, a goal that cannot always be achieved with frozen solvents. By this token, noble gases, especially neon and argon, are clearly the best choices, although in many cases the heavier noble gases, nitrogen, methane, or other inert molecular hosts, may also be used. On the other hand, one may want to deliberately choose a matrix material that is *reactive* toward the targeted intermediate, for example, CO or O₂, to trap carbenes or nitrenes, but that preserves the other advantages over polyatomic solvents (see below). Often, doping of an inert host material with an additive that fulfils a certain function (e.g., an alkyl chloride that can trap electrons when one wants to study radical cations), or can enter into diagnostic reactions on annealing (see below) is the strategy of choice.

Frozen solvents have another disadvantage, namely, that they are often opaque throughout wide regions of the infrared (IR) and part of the UV spectral range. Since vibrational spectroscopy can provide (at least potentially) much more structural information than UV-vis spectroscopy, this creates an incentive to generate reactive intermediates in a medium that allows their observation in the IR. Since all atomic and homonuclear diatomic gases are entirely transparent in the IR (and in most cases also throughout the visible and UV), they also represent ideal choices as matrix hosts also from this spectroscopic point of view. Actually, these materials have the additional advantage that they offer generally much higher spectral resolution (i.e., narrower bands) than frozen solvents, which can be a decisive factor if it comes to disentangle complex spectral patterns. The spectra of the naphthalene radical cation in a frozen mixture of butyl chloride (BuCl) and isopentane (iP) at 77 K,⁷ and in an Ar matrix at 12 K⁸ shown in Figure 17.1 may serve to illustrate this feature, as well as the extended observational range in the UV.

A third advantage that matrix isolation has over frozen solvents is that the reactive intermediates must not necessarily be generated *in situ*, but can be made by flash vacuum pyrolysis or in plasma processes prior to their quenching with an excess of the host gas on the cold surface. Of course, this considerably widens the range of reactive intermediates that can be investigated, beyond those that require photolysis or some form of radiolysis for their formation.

Finally, because very low temperatures are needed to solidify the above host gases, reactive intermediates may be generated under conditions where unimolecular thermally activated processes are also largely suppressed, unless they involve quantum mechanical tunneling. Thus, species that rearrange or fragment spontaneously even at 77 K can be stabilized, say, at 10 K, provided that such processes are not driven by excess energy that is imparted onto the incipient intermediates on their formation by photolysis or radiolysis (see below).

Thus, there are many good reasons why someone who is interested in studying reactive intermediates may want to purchase the necessary equipment and go to the trouble of familiarizing himself or herself with the technique of matrix isolation.

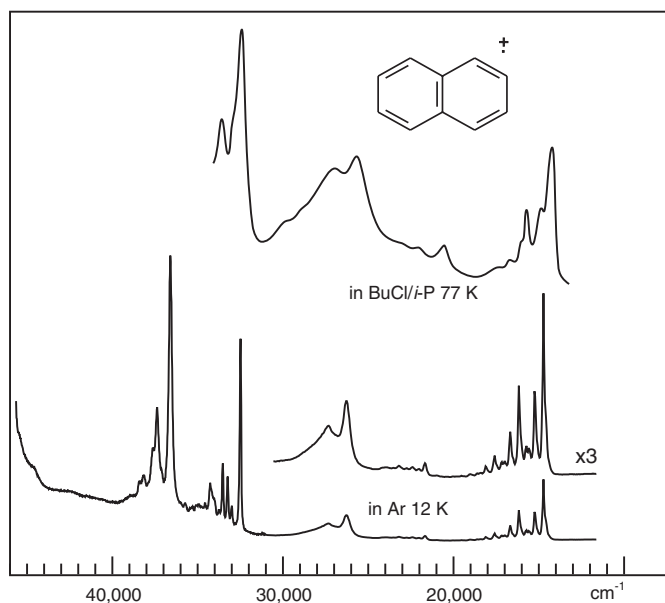


Figure 17.1

In fact, as will be shown below in Section 3, this has become much less daunting than it used to be in the early days.

3. LIMITATIONS OF MATRIX ISOLATION

It is of course important to realize that the technique of matrix isolation also has its limits, or that certain conditions must be fulfilled so that it can be applied. The first and most important one is that the precursor of the reactive intermediate to be studied must be an isolable substance and volatilizable without decomposition, which sets limits on the size of species that can be studied and/or on their thermal lability. Thus many interesting compounds (e.g. of biological relevance) are excluded, at least in their native forms. Also very nonvolatile substrates, such as metals, require special techniques such as Knudsen cells for controlled evaporation.

Second, rich bimolecular chemistry (attack by nucleophiles, electrophiles, oxidants, or reductants) that can be used to create reactive intermediates in solution is not generally available in the context of matrix isolation (exceptions to this rule will be discussed in the proper context below). Usually, reactive intermediates to be studied by matrix isolation must be accessible by means of unimolecular processes (fragmentations, rearrangements, ionization) induced by external sources of energy (light or other forms of radiation, discharges).

Third, even precursors that readily provide some reactive intermediate in solution or in the gas phase, will not necessarily “work” inside a matrix because of the

so-called *cage effect*. With the exception of hydrogen and fluorine atoms, all fragments that might be created during the cleavage of a precursor will usually remain trapped in the same matrix cavity and may therefore undergo recombination, either in very low activation thermal processes or driven by (inadvertent) excitation of the target intermediate. Thus, a precursor that undergoes efficient photocleavage in solution or in the gas phase may appear to be entirely photostable under matrix conditions, simply because the fragments recombine immediately after their formation.

A fourth, often overlooked problem is most prominent in noble gas matrices which are notoriously poor heat sinks because only very low energy lattice phonons are available to accept molecular vibrational quanta. Hence, thermalization is very slow compared to solution, and the excess energy that may be imparted onto an incipient reactive intermediate in the process of its formation (e.g., from a precursor excited state) may therefore be dissipated in secondary chemical processes such as rearrangements or fragmentations, which may make it impossible to generate the primary reactive intermediate. Often, this problem can be alleviated by attaching alkyl groups that serve as "internal heat sinks," but sometimes this is not acceptable for other reasons.

Finally, one should pay attention to the fact that especially polar substrates have a tendency to form dimers or higher aggregates, even in the gas phase (although that tendency is much smaller than in frozen solutions). Thus, on radiolytic ionization of anthracene evaporated into a stream of Ar and trapped at 20 K a sizeable yield of the dimer cation is obtained, indicating that at least a part of the anthracene sample exists in the gas phase and later in Argon in the form of dimers. Another classical example is diazocyclopentadiene, which invariably yields a fulvene (the dimer of the targeted reactive intermediate, cyclopentadienylidene) on photolysis in matrices. Going to higher host/guest ratios may diminish or eliminate aggregation of precursors in the gas phase, but often this is not practical due to the ensuing loss of spectroscopic signals. A simple trick is to pass the stream of gas through a tube immersed into an ultrasound bath, thus providing energy to separate aggregates before deposition on the cold surface.

4. TECHNICAL ASPECTS, EQUIPMENT

When matrix isolation was invented in the 1950s, carrying out such experiments required a degree of adventurousness, because it involved the handling of liquid hydrogen or helium in open Dewar vessels, and stories of much destroyed laboratory equipment are recounted by people who were active in the field in its pioneer heydays. Luckily, matrix isolation is nowadays no riskier than any other standard laboratory activity. It requires mostly commercially available equipment that has undergone many cycles of improvement and is functioning reliably. Nevertheless, competent support from a machine shop and a glass blower is of great help to set up a laboratory for matrix isolation, as will become evident in the following sections that will be devoted to short descriptions of the different pieces of equipment required to carry out matrix isolation experiments. For more detailed information,

and for many helpful practical hints, the reader is referred to the excellent guide by Dunkin.⁹ Where it goes into detail, this chapter will focus on aspects that are not covered in the above book.

4.1. Cryostats and Associated Apparatus

Unless temperatures below 10 K are required for the condensation of the host gas or to prevent some low-activation thermal process from occurring, a *closed cycle cryostat* will invariably form the heart of each matrix isolation setup. These devices, which brought matrix isolation also to laboratories with no (affordable) access to liquid helium, consist basically of a compressor and an expander, connected by two lengths of high-pressure steel bellows tubing. Helium is used as the working medium in a so-called Gifford–McMahon cycle to generate temperatures down to 10 K at the cold end of the second stage of the expander (with special regenerator materials in the second stage of the expander down to 6 K may be attained, if needed).

If one intends to use Ne or H₂ as a host gas, one needs to take recourse to cryostats that are able to attain temperatures of 4 K or less. Until recently, *flow cryostats*, where liquid He is guided in a controlled fashion to the cold end, were usually required for such experiments. However, two-stage 4 K closed-cycle cryostats have recently become available that appear to obviate the need for liquid He.¹⁰ The author knows of two prominent matrix-isolation research groups who have been using such devices for a little while now and have no complaints about them.

During sample deposition, or in annealing experiments, one does not want to operate a cryostat at the lowest temperature it can attain. Rather than reducing the cooling power of the cryostat, this is achieved by fitting the cold end with a resistive heating element and a thermocouple or a silicon diode. Higher temperatures are then attained by passing variable amounts of current through the resistive heater, a task that is usually handled by an electronic device that can be programmed to assure that a chosen temperature is maintained in the presence of varying heat loads without undue oscillations due to temporary under- or overheating. Most suppliers of cryostats will be able to provide expanders that are fully equipped and ready to cooperate with one or another temperature controller. For little additional cost, they will also mount an extra thermocouple or silicon diode that can be connected to a spare channel of the temperature controller and may be used, for example, to monitor the temperature directly in the sample, where it is usually a few degrees higher than directly on the cold end of the expander.

Of course all surfaces that are at such low temperatures must be kept out of contact with the ambient environment. This is achieved by a detachable and rotatable *vacuum shroud* that surrounds the two expander stages and the sample, all of which must be kept under high vacuum while they are cold to avoid *collisional heat transfer*. By default, evacuation of the assembly occurs through vacuum ports mounted on the main body of the expander, but in some cases it is advantageous to have extra ports on the vacuum shroud itself. Furthermore, the first expansion stage of closed-cycle cryostats, where a temperature of ~35–40 K is attained, is usually fitted with

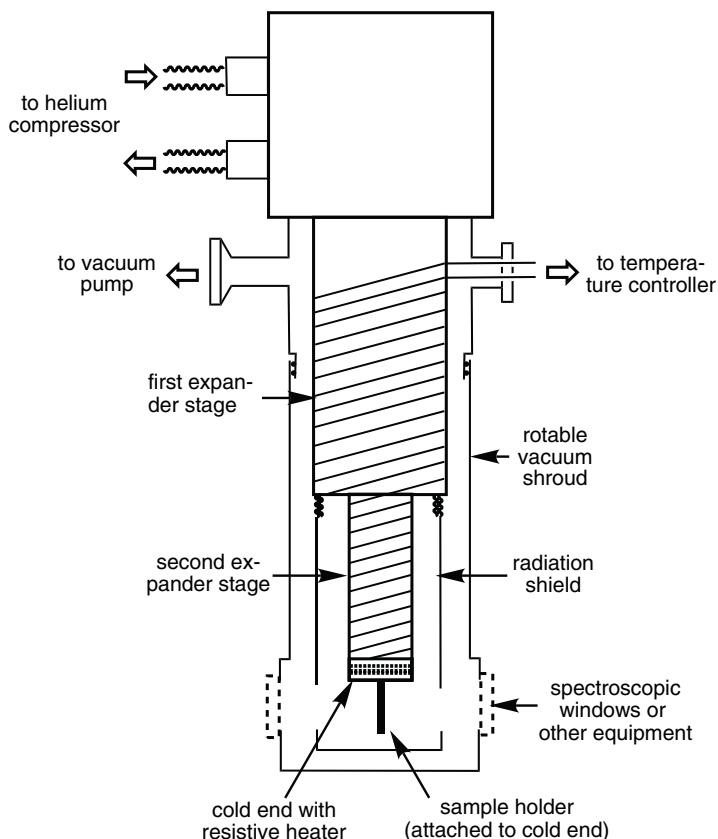


Figure 17.2

a detachable *radiation shield* that extends over the length of the second stage and the sample to protect both from *radiative heat transfer*.

The part of the vacuum shroud that surrounds the sample has several openings fitted with O-rings and threaded holes. These openings can be equipped with spectroscopic windows, different inlet systems, sources of high-energy radiation such as open discharge lamps, or other devices. Some suppliers will furnish window holders, and ARS even equips their vacuum shrouds with small side ports that can be used as sample inlet systems, which are not very practical in many cases. Most users will, however, want to customize the equipment to be mounted on the shroud openings such as to optimally serve their particular uses. Figure 17.2 shows a schematic drawing of a typical closed-cycle cryostat (minus the compressor).

4.2. Sample Holders, Spectroscopic Windows

The sample holder designates the body on which the matrix is deposited, and its interface to the cold end of the cryostat. The choice of that body depends on the

type of spectroscopy that one wants to use. If one is only interested in UV-vis/NIR (near-infrared) absorption spectra, then a sapphire or well-polished CaF_2 disk are most appropriate.¹¹ Since one of the major advantages of matrix isolation (as compared to frozen solvent studies) is that IR spectra of reactive intermediates may be recorded, one will usually want to choose a material that is also transparent in this spectral range. Even if the full range of its IR transparency (down to 200 cm^{-1}) is not exploited, *cesium iodide* is the best choice, mainly because of its advantageous mechanical properties: NaCl and KBr crystals are so brittle that the mechanical stress during their cooling and heating over a range of nearly 300 K, while being fitted tightly into a copper ring of different expansivity, will often lead them to crack or cleave. In contrast, CsI behaves like a soft glass and weathers most conditions that occur in matrix isolation experiments. However, CsI is also very hygroscopic, and therefore one has to wait after every experiment until the sample holder has returned to ambient temperature before exposing it to atmosphere, to prevent condensed water from dissolving the precious material.

In contrast to popular belief, nourished by poorly maintained solution IR cells, well-polished alkali halide crystals are transparent down to 200 nm, so it is usually no problem to take UV/vis and IR spectra from the same samples deposited on CsI windows. One should, however, request the slightly more expensive "UV-quality" material that is free of color centers in this spectral range. Buying polished crystals is not worth the considerable additional expense, because one has to set up a facility for polishing them after each use anyway. In our experience, a soft suede leather cloth stretched over a glass slab and a bottle of isopropyl alcohol is all that is needed for this purpose, although crystals with coarsely ground or very foggy surfaces may need some pretreatment with very fine wetted sandpaper, followed by some wiping with water and ethanol, before polishing with isopropyl alcohol becomes effective.

Similarly, fused silica windows are not required except for the most demanding applications in UV spectroscopy, so fitting the vacuum shroud with a pair of well-polished KBr windows is usually appropriate,¹² unless one needs IR transparency at $500\text{--}200\text{ cm}^{-1}$, when one has to use CsI windows. If one needs to probe the far-IR range ($<200\text{ cm}^{-1}$) one has to use polyethylene windows (the covers that come with KF flanges have proven adequate), but this makes it of course impossible to probe the same samples in the mid-IR or UV-vis range.

One of the most frequent reasons for failures of matrix isolation experiments is inefficient heat transfer between the sample and the cold end of the cryostat. Thus, it is very important to assure good thermal contact between the window and its holder (which must be made from a material of high heat conductivity), and between the latter and the cold end. This good thermal contact is effected by sandwiching the window between two copper plates fitted with indium O-rings that are flattened when the screws that hold the plates together are tightened.¹³ Similarly, indium washers placed between the window holder and the cold end of the cryostat make sure that heat flow across this junction is not impeded. Figure 17.3 shows such a sample holder for optical absorption studies.

If one wants to measure spectra in *reflection*, the task of building a sample holder is much simpler, because it can be machined in one piece from solid copper that

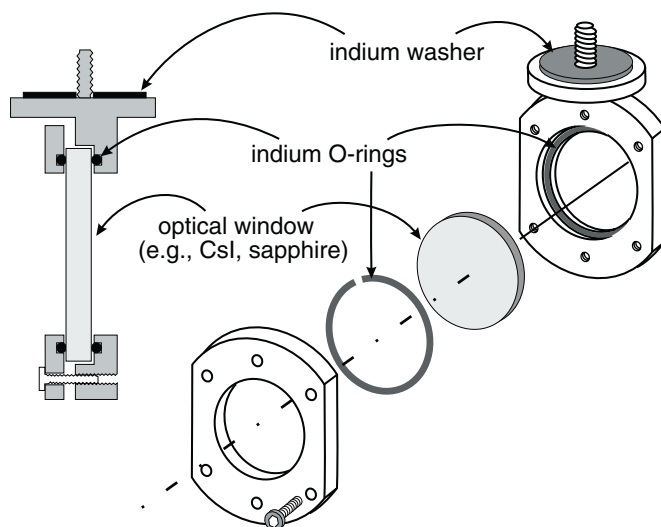


Figure 17.3

eliminates the above mentioned heat-transfer problems. For UV–vis studies the surface should be plated with nickel or silver, whereas in the IR a coating of gold assures optimal reflectivity. Similar sample holders may also be used for Raman scattering studies.

An interesting variant of a reflective sample holder that can be used both for absorption and emission studies was proposed by Rossetti and Brus.¹⁴ They mounted two $\sim 100\text{-}\mu\text{m}$ slits on the edges of a mirrored plate and deposited a matrix to cover these slits. When one focuses a beam of exciting or probe light onto one of these slits, the mirrored surface and the matrix serve as a *waveguide* by internal reflection, and the light emanates from the opposite slit with very little loss. This technique allows absorption measurements on very dilute samples because the optical pathlength ($\sim 2\text{ cm}$) is two orders of magnitude longer than the thickness of a typical matrix ($\sim 200\text{ }\mu\text{m}$). The same setup can be used to excite a sample (e.g., by a laser) and collect emitted light perpendicularly.

A wholly different setup is required for ESR studies of matrix isolated open-shell species, because the cavities of ESR spectrometers are too narrow to accept the standard vacuum shrouds. Therefore, these shrouds have to be fitted with a small extension tube at the bottom into which a sapphire rod can be lowered after the gas sample mixture is deposited on that rod. This modification requires in turn a special shroud that can be raised and lowered without breaking the vacuum. Such equipment is available commercially and is described in various books and reviews on matrix isolation.

4.3. Inlet Systems

If all that is required is the passage of a mixture of the host gas and the substrate from the sample preparation line onto a cold window, the inlet system can consist of a simple glass tube extending from the high vacuum side of a teflon valve through a Cajon ultratorr fitting that is welded onto a plate covering one of the free openings of the vacuum shroud. The ambient pressure side of the valve should provide for a connection to the sample preparation vacuum line (an example of such a setup is given in Fig. 17.4).

Substrates that are not sufficiently volatile to be premixed stoichiometrically with the host gas have to be placed in a U-tube that can be immersed into a temperature-controlled bath. A stream of host gas passing through this tube will then sweep the substrate along and form a mixture whose ratio depends (at a given geometry and substrate surface) on the temperature of the bath.^{15a}

For substances that require more than $\sim 50^\circ\text{C}$ for slow evaporation, a furnace must be attached directly to the vacuum shroud. A very simple solution, proposed by Tomioka,^{15b} consists of a double-walled glass tube that fits into a steel tube

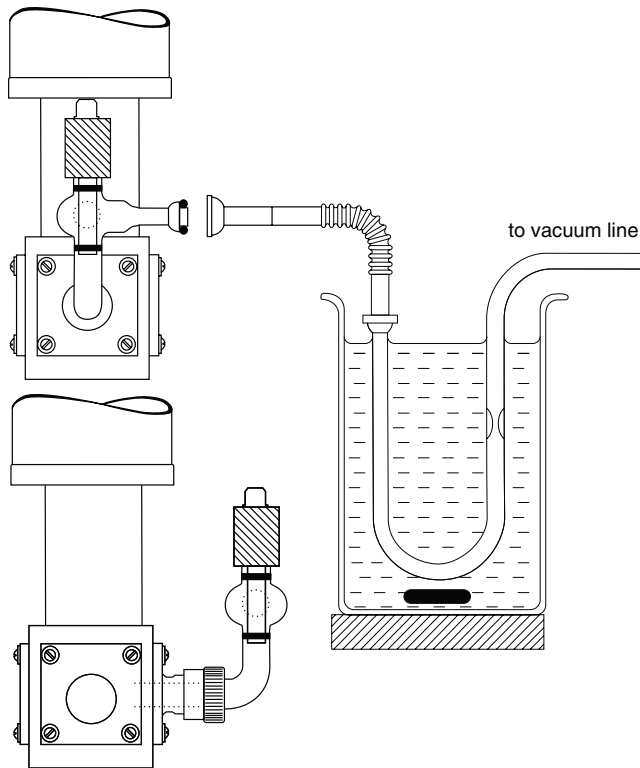


Figure 17.4

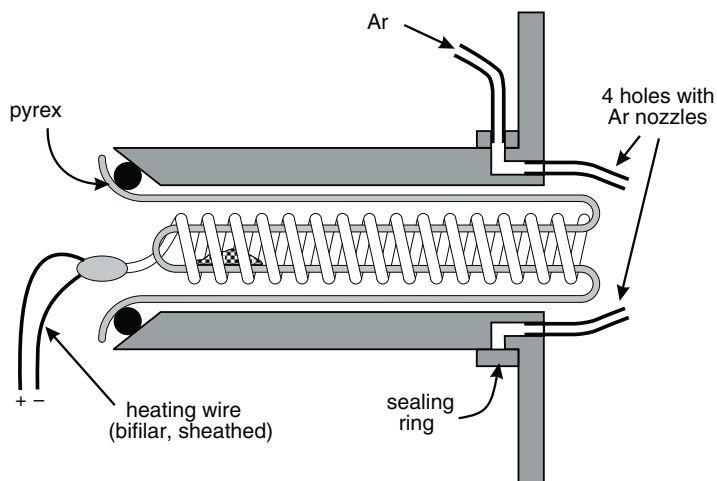


Figure 17.5

attached to a plate (cf. Fig. 17.5). The substrate is placed in the inner part of the glass tube that opens toward the sample window and that can be heated resistively up to ~ 300 °C. The host gas must be introduced separately, in a way that allows its efficient mixing with the substrate emanating from the heated tube. In the author's laboratory, a design with four small nozzles placed symmetrically around opening of the hot tube has proven suitable for this purpose (see Fig. 17.5). If higher temperatures are needed to volatilize a substrate, one must resort to Knudsen cells.

More elaborate setups are required if the target reactive intermediate is generated by pyrolysis or by passing the precursor through a microwave or electric discharge. The most clean and efficient pyrolysis can be achieved by a technique of pulsed deposition of the substrate–host gas mixture through a very hot ceramic tube. The design of such a system has been described by Chen and co-workers,¹⁶ and variants thereof have found application in several matrix isolation laboratories. Many designs of such “functional” inlet systems that allow substrates to be deposited at high temperature or by sputtering, or pyrolysis, or after being subjected to discharges, or exposure to far-UV light or to beams of electrons are described in detail in the book by Moskovitz and Ozin,¹⁷ so we will not go into more detail here, but refer to some of them in the context of the different techniques for the generation of reactive intermediates (Section 5).

A major problem with “functional” inlet systems is that they are often quite bulky, which makes it difficult to move the cryostat from the sample deposition line to different spectrometers, or from there to stationary sources of radiation. If only one form of spectroscopy is applied in a given study, then the vacuum shroud may be mounted with all parts attached to it in the sample chamber of the corresponding spectrometer. In this case the expander, on which the sample holder is attached, must be rotated within the vacuum shroud to switch the sample from

matrix deposition to observation. Another solution is to design the inlet system in such a way that it can be detached from the vacuum shroud after deposition, thus restoring full mobility to the experiment, but this may be tricky because high vacuum must be maintained at all times inside the shroud. However, with the help of compact gate valves mounted on the one of the shroud's openings such solutions can be realized.

4.4. Sample Preparation Lines

The sample preparation vacuum line (often called "spray-on line") should allow for (a) controlled mixing of the host gas with the substrate (or with other components that are added to the matrix) by manometric techniques and (b) the controlled release of the gas (mixture) toward the inlet system of the cryostat. These conditions are met by a vacuum line that incorporates a storage bulb for the gas (mixture), inlets for attachment of evacuable containers that allow degassing of the substrate prior to its mixing with the host gas, pressure gauges that cover suitable ranges, a needle valve that allows the controlled release of the gas, possibly via a flowmeter, and interfaces to the bottles that contain the host gas(es), and to the inlet system that is attached to the vacuum shroud of the cryostat.

Suggestions on how to build and equip such vacuum lines are given in Dunkin's book,⁹ so no details will be given here. Note that careful degassing of the sample prior to evaporation of the substrate, which needs to have a vapor pressure of at least 0.1 Torr to allow premixing with the host gas, is very important to assure good control over the host/guest ratio that should be kept below 1:500 to allow good isolation in the matrix.

4.5. Vacuum Equipment

High-vacuum pumps are needed, both for the evacuation of the cryostat and for the sample preparation line. In some laboratories, the same pumps are used to serve both purposes, but this entails several disadvantages, such as bellows tubes leading from the vacuum line to the cryostat that make for very inefficient pumping in the low-pressure regime. Since the volume of the cryostat is quite limited, even a very compact vacuum pump serves well for its efficient evacuation, provided that losses of pumping efficiency can be avoided. Several suppliers now feature small turbomolecular pumps (pumping speeds of 50–100 l N₂/min suffice largely) that can be mounted horizontally, that is, flanged on in line with the expander port. Such pumps obviate the need for constructing complicated manifolds and at the same time minimize losses of pumping efficiency. Backing by a small rotary or membrane pump completes the vacuum system.

In order to avoid having to shut down the whole vacuum system each time the cryostat is vented after an experiment, it is advisable to place a small slide or butterfly valve between the turbopump and the expander port. When the system is reevacuated, the turbopump must be stopped before opening the valve, otherwise the ambient pressure shock wave that results might deform the delicate rotor and

stator blades. However, one advantage of these small turbopumps is that they do not need to be bypassed for roughing, which simplifies the design of the vacuum system.

Once the cryostat has attained about 40 K, the cold end of the expander is the most efficient vacuum pump for ambient gases in the system, and external evacuation is no longer required (i.e., the cryostat can in principle be detached from the vacuum system). Nevertheless, most practitioners of matrix isolation prefer to keep up the pumping, be it only to continue monitoring the pressure inside the cryostat (Penning gauges may give erroneous readings in closed-off systems).

The choice of vacuum pumps for the sample preparation line will depend on the size of its volume and the budget. In general it is advantageous to have somewhat higher pumping speeds available for the vacuum line, but this can well be provided by a conventional oil diffusion pump, which is less expensive than a turbomolecular device, backed again by a rotary pump.

4.6. Trolleys

Unless a matrix isolation experiment is built into or around a spectrometer (which may be the only way to go if, say, a bulky inlet system has to be interfaced to the cryostat), the entire cryostat and the associated vacuum pumps (which together may easily weigh in at more than a hundred pounds) should be mobile in order to move them between different locations in a laboratory. The challenge then consists in constructing a device that will not only allow the whole setup to be wheeled around without too much effort, but permits also a precise and reproducible positioning of the sample next to the sample preparation line, inside different spectrometers, or in front of this or that external source of radiation. Ideally, one should be able to move the expander in all three directions of Cartesian space, at least within certain limits, without having to change the position of the cart or trolley on which the equipment is mounted.

When compact X-ray sources became available in the late 1970s, many dentists unburdened themselves of the somewhat unwieldy cranes that were required to position the older heavy devices next to their client's faces to obtain X-rays of their teeth. However, these cranes had precisely the features that are required for a good matrix isolation trolley, that is, the capability to position a rather heavy piece of equipment precisely in space without much physical effort. In the author's laboratory several such cranes have served (and continue to serve) splendidly for this purpose, and any potential practitioners of matrix isolation are well advised to keep their eyes open for such a device, some of which may still be had for free if they have not already been discarded.

Otherwise the construction of a trolley requires competent professional help. Once more, Dunkin's book⁹ may serve as an excellent source of information to get started, although one may want to adapt the designs proposed therein to local circumstances. In any event, it pays to invest in the careful design of the trolley, because this can make life in the laboratory much easier afterwards!

4.7. Spectrometers

Advising the reader on the choice of spectrometers is of course beyond the scope of this chapter, but we would like to point out some features that are worth considering when purchasing or adapting such equipment for the purpose of matrix isolation experiments. In all cases, it is worthwhile to look for spectrometers that have spacious sample compartments, or are constructed in such a way that the probe beam can easily be deflected out of the spectrometer for passing through the sample, and then back toward the monochromator or detector. Usually one will find that the cover of the sample compartment must be dismantled to gain access with the cryostat, and often one will want to replace it with a customized cover to close off the compartment for purging, or to shield it from ambient light while the sample sits in there. Some spectrometers now come with fancifully shaped sample compartment covers that are not easily amenable to modification or replacement, so this should be kept in mind when considering the purchase of a spectrometer.

Whereas purging is usually not required for UV-vis spectrometry, it is inevitable in IR work, because the sharp bands of gaseous H₂O and CO₂ (whose shape is very sensitive to pressure and temperature), never cancel completely on ratioing sample and reference spectra, partly because the volume inside the vacuum shroud is completely free of these gases. The optimal solution to this problem is to evacuate the entire spectrometer, including the sample compartment, before taking IR spectra of matrix isolated species. Unfortunately, evacuable Fourier-transform infrared (FT-IR) spectrometers tend to be on the upscale side, but if one can afford such an instrument, then one never has to worry about dwindling nitrogen supplies on humid summer days or foggy beamsplitters. Instead, one has to design a special cover with a vacuum seal for the cryostat, but the author will gladly supply information on how to go about that.

One of the greatest advantages of matrix isolation IR (or Raman) spectroscopy is that vibrational bands are inherently very narrow, because rotations are largely suppressed, which means that much more detailed information can be obtained than in the liquid phase at room temperature. However, this additional information can only be obtained if the spectrometer offers high enough resolution, which in the case of interferometers translates into sufficient displacement of the movable mirror. For most practical purposes, a resolution of 1 cm⁻¹ is adequate for matrix work, although it is good to have 0.5-cm⁻¹ resolution available in case one needs it, say, for the elucidation of site structures.

Finally, in our age of powerful electronics, it is often forgotten that the most sophisticated signal conditioning circuitry or data handling software is no replacement for good optics and precise mechanics. Unfortunately, there is a price to be paid for the latter and the reason for the additional expense only becomes evident to a trained eye after opening the cover of the spectrometer, so the temptation is great to settle blindly for a more economical solution. Engaging in a news group of scientists who exchange technical information, and seeking the advice of colleagues who use this or that spectrometer for similar purposes, may help to avoid disappointments.

5. METHODS FOR GENERATING REACTIVE INTERMEDIATES FOR LOW-TEMPERATURE MATRIX STUDIES

Principally, there are three ways to generate reactive intermediates for matrix isolation studies, each of which has its own range of application, advantages, and limitations. They are

1. External generation followed by trapping in the matrix.
2. Cocondensation of a precursor with a reagent with which it will react in the matrix (usually during the condensation process).
3. Generation from a precursor isolated in the matrix (i.e., *in situ*).

These three methods will be highlighted briefly below.

5.1. External Generation

If the experiment is conducted properly, this method has the advantage that the reactive intermediate to be studied is truly isolated in the sense that it is (ideally) surrounded by nothing but the inert host material (doped perhaps with some deliberately added reagent). This feature can be very important, say, in the case of radicals which usually arise in pairs that have a propensity to recombine if trapped in the same matrix cavity, which often excludes method (3) above for the generation of such species.

On the other hand, external generation of reactive intermediates has two potential disadvantages, a chemical and a technical one. First, the target reactive intermediate must persist during the time that passes between its creation and its thermalization in the cold matrix environment. Thus, species that are prone to undergo thermal rearrangements or fragmentations at the temperature that prevails in the environment where they are generated (say, a pyrolysis or discharge tube) will not appear in the form of the primary reactive intermediate in the matrix. For example, any attempt to study the radical cation of cyclobutene generated externally by matrix isolation is bound to fail because this species will have rearranged to the butadiene radical cation by the time it has reached the matrix. Similar considerations apply, for example, to carbenes carrying α -hydrogen atoms.

Second, contraptions used for external generation of reactive intermediates are often quite bulky, which may impede the mobility of the experiment. Such contraptions may render it difficult to investigate a sample by several different kinds of spectroscopy. In principle it is possible, with the aid of a gate valve mounted on the vacuum shroud, to construct devices that allow one to retract and detach the external source of a reactive intermediate after a matrix has been built, but the implementation of this strategy is technically quite challenging because high vacuum must be maintained at all times within the cryostat.

The methods for external generation of reactive intermediates are similar to those used in gas-phase experiments, that is, flash vacuum pyrolysis, passing a

precursor through a microwave discharge, electron or proton radiolysis, or far-UV irradiation with open-tube discharge lamps during deposition (whereby most far-UV light is absorbed by gas-phase molecules excited into Rydberg states). Where necessary, details of these methods will be described in connection with their use to make different types of reactive intermediates in the following sections.

5.2. Cocondensation of Two Reagents

This method has been used very successfully by many groups, especially in the field of inorganic and organometallic chemistry. Typically, a beam of metal atoms, generated by evaporation from a high-temperature furnace (Knudsen cell), or by laser sputtering, is fed into a beam of the host material mixed with a compound whose adduct with the metal atom is the targeted reactive intermediate. For example, the group of Andrews has made quite a living over the past years from cocondensing a variety of transition metal atoms and clusters, obtained via laser sputtering, with H_2 ,¹⁸ N_2 ,¹⁹ O_2 ,²⁰ CO ,²¹ CO_2 ,²² H_2O ,²³ NO ,²⁴ or S vapor²⁵ (only the most recent references are given). However, the same can be done with nonmetals, most importantly carbon (cf. Chapter 10 in this volume) or silicon.

The setup used in these experiments is remarkably simple: all that is required is a mechanical vacuum-feedthrough by which a rotatable rod, made of or topped by the desired material, can be introduced. Pulses of the fundamental of a Q-switched, pulsed Nd:Yag laser (typically 20–80 mJ/pulse, 1–10 Hz) are focused on that target, either through a separate port,²⁶ or simply from behind the cold window.²⁷ In order to avoid formation of pits that lead to a greater propensity for cluster formation, the rod is rotated slowly such as to expose a fresh surface to successive laser pulses.²⁸

On the other hand, alkali metal atoms can be obtained by simple evaporation at moderate temperatures, and these may serve to abstract bromine or iodine from organic halides, thus providing access to radicals,²⁹ biradicals,³⁰ or highly strained hydrocarbons, such as small-ring propellanes.^{31,32} The technique has been described in some detail by Otteson and Michl.³³

Matrix-isolated alkali atoms (or small clusters) also undergo easy photoionization, and the electrons released in this process may attach themselves to nearby substrates to form the corresponding radical anions.³⁴ However, one drawback of alkali metal atoms or clusters is that they tend to swamp the electronic absorption spectrum of the target reactive intermediate that can only thus be detected by IR.

An interesting variant of method (2) was discovered some time ago by Jacox who found that passing a mixture of NF_3 or CF_4 with Ar through a microwave discharge gave a high yield of fluorine atoms which could be used to abstract hydrogen atoms or add to multiple bonds or lone pairs.³⁵ However, since F atoms may diffuse through an Ar matrix, especially at a time when it is not yet completely solid, most of the products appeared in the matrix as complexes with HF, which often gave rise to rather substantial shifts of vibrational transitions compared to the free radicals.

5.3. Generation *In Situ*

Finally, *in situ* generation is by far the most popular method for the preparation of many types of organic reactive intermediates, because it is usually easiest to implement and does not impede the mobility of the experiment. Furthermore, the design of suitable precursor molecules often offers an interesting challenge to the synthetic chemist. Invariably, the energy required for the generation of a reactive intermediate from a precursor that is already embedded in a matrix comes in the form of *electromagnetic radiation*. In the case of neutral intermediates, this will usually be near UV light such as that provided by the widespread Hg, Xe, or Hg/Xe arc lamps. Often judicious filtering is required to avoid unwanted secondary reactions, or sometimes lasers are even employed to ensure monochromatic irradiation at a desired wavelength.

If direct *ionization* of a substate is to be effected, higher energy light is required, which can be generated by so-called resonance lamps where a suitable gas is enclosed in (or flowing through) a tube, capped with a LiF or MgF₂ window, where it is excited in a microwave discharge. Wavelengths between 122 nm (H₂) and 175 nm (N₂) can be obtained in this way, and tables for different gases have been compiled.³⁶ and are reproduced in some books on matrix isolation techniques.¹⁷

Although irradiation of a matrix will usually be effected at an energy where the targeted precursor shows some optical absorption, this is not invariably a prerequisite to achieve an effect on this precursor. For example, matrix-isolated organic radical cations can be generated by irradiation of Ar matrices by X-rays (to which molecules containing only second-row atoms are practically transparent) whereby the host material is ionized. Subsequent hole transfer to an added substrate leads to the formation of substrate radical cations³⁷ (see Section 5.6). Also, Maier and Lautz³⁸ recently found that 254-nm irradiation of Xe matrices doped with halogen atoms leads to bond cleavage in alkanes or olefins that do not absorb (and are otherwise photostable) at this wavelength. The mechanism whereby the energy that is primarily stored in Xe · Br complexes is transferred to the hydrocarbons has not been elucidated, but this method has allowed researchers to achieve some remarkable transformations.

If *in situ* generation of a reactive intermediate involves the formation of fragments, which is often the case, then one has to consider that these will be trapped in the same matrix cavity. With few exceptions (H and F atoms), the fragments will not be able to separate by diffusion through the matrix, so their recombination may occur more or less readily, depending on the activation energy for this process and geometric factors that may come into play. This so-called *cage effect* is especially obstructive in the formation of radicals which usually arise in pairs that may recombine with little, if any, activation energy. For example, certain binuclear metal carbonyls that readily undergo cleavage of the metal–metal bond on photolysis in solution, thus yielding reactive intermediates that undergo further interesting chemistry, appear as entirely photostable or undergo only loss of CO in matrices, due to the rapid recombination of the primary fragments. Further manifestations of the cage effect will be illustrated in the following sections.

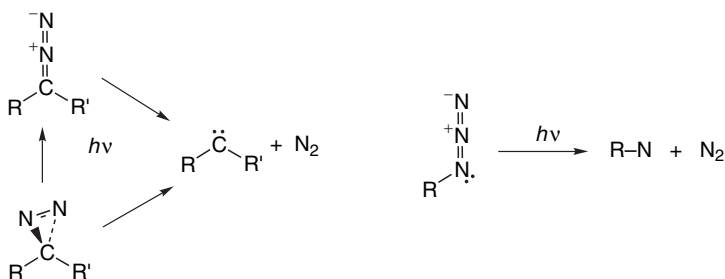
Another potential limitation of *in situ* generation of reactive intermediates is that they must be reasonably photostable under the conditions of irradiation required for their generation. The higher the energy of the light that is needed to decompose a precursor, the more likely it is that the resulting intermediate is also affected by that light. Thus, phenol, which is in principle a very good precursor of the phenoxy radical because the hydrogen atom that is formed concomitantly can escape by diffusion through most matrices, gives the decomposition products of the phenoxy radical ($\text{CO} + \text{C}_5\text{H}_5$) as major products on 254-nm irradiation in Ar matrices.³⁹

However, the cage effect may allow an investigator to monitor processes that cannot be observed in the gas phase or in solution because fragmentation prevails under these conditions. A good example are radical cations which usually undergo dissociation on photoexcitation in the gas phase,⁴⁰ but that display a rich variety of photorearrangements in Ar matrices.³⁷

6. PREPARATION OF DIFFERENT TYPES OF REACTIVE INTERMEDIATES

6.1. Carbenes, Nitrenes

The great majority of matrix isolation studies of carbenes and nitrenes have employed their formal adducts with molecular nitrogen, that is, diazo compounds or diazirines in the case of carbenes, azides in the case of nitrenes, as precursors for their *in situ* generation. Usually, these compounds will readily release N_2 on irradiation with a low-pressure mercury lamp (254 nm), and this fragment has the advantage that it will usually not react with or perturb the targeted reactive intermediate (see Scheme 17.2).



Scheme 17.2

A notable exception to this rule is the parent carbene (CH_2) whose characterization as a matrix isolated species was impeded for a long time because it recombines readily with N_2 , even at 10 K, as demonstrated by the exchange of ^{15}N against ^{14}N when isotopically labeled diazomethane was photolyzed in a N_2 matrix.⁴¹

From the *singlet* state of CH_2 , this recombination is exothermic by about 35 kcal/mol,⁴² and, according to calculations, it should proceed with no barrier.⁴³ However, it would be surprising if all CH_2 would be trapped by N_2 before it undergoes intersystem crossing to the triplet ground state, which is thermally unreactive toward N_2 at matrix isolation temperatures. Perhaps the recombination is due to excitation of $^3\text{CH}_2$ under the conditions where diazomethane is decomposed. Photoinduced recapture of N_2 by carbenes has also been reported for cyclopentadienylidene and 2,5-diazacyclopentadienylidene (the latter is a singlet carbene which also adds N_2 thermally on annealing a matrix to 25 K).⁴⁴

Diazo compounds are usually easy to synthesize and handle if the N_2 group is next to a carbonyl or an aryl group. In other cases, especially when electron-releasing substituents such as halogen or oxygen atoms are adjacent to the diazo moiety, diazirines prove to be more practical. Sometimes, diazirines undergo photorearrangement to diazo compounds prior to decomposition (or vice versa, as in the case of phenyldiazomethane⁴⁵), but this does not impede the formation of the desired carbene.

A disadvantage of diazo compounds is that they are quite polar, which endows them with a propensity to form dimers in the gas phase, even at concentrations as small as 1:5000. This feature becomes evident after their decomposition, which sometimes leads predominantly to carbene dimers (e.g., pentafulvalene in the case of diazocyclopentadiene⁴⁶), or adducts of the target carbene with its diazo precursor, as in the case of methylene, where the main products are $\text{CH}_2=\text{NH}$ and HCN .⁴⁷ The problem disappears at very high guest/host ratios, but it is often impractical to achieve these. Fortunately, diazirines are less prone to dimerization in the gas phase.

Other possible carbene precursors (vicinal dihalides, peresters, ketenes, carbene adducts with stable hydrocarbons, etc.) cannot generally be used for *in situ* generation of carbenes, because the fragments are likely to recombine. However, they can be used, for example, in experiments involving pyrolysis or other forms of external carbene generation where the fragments get a chance to separate in the gas phase and become trapped in distant matrix sites. All conceivable halo- and dihalocarbenes were made and studied in this way (see, e.g., the 1993 review by Sander et al.⁴⁸) However, such methods can only be applied to carbenes which resist thermal rearrangement to more stable products.

Azides are virtually the only nitrene precursors that have been used in matrix isolation studies. They are usually easily accessible, but should only be made and handled in very small quantities because certain azides can be violently explosive.

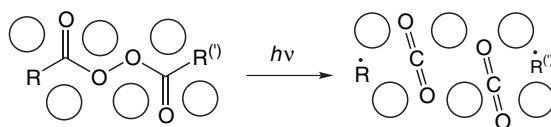
6.2. Radicals

The cage effect can be a source of great frustration in matrix isolation studies of monoradicals, because such species are usually formed by homolysis from closed-shell compounds, and hence any radical generated *in situ* is invariably accompanied by another radical that will be trapped in the same matrix cage.

Hence, most photochemical precursors of radicals in solution (peroxides, azo compounds, most halides, etc.) are not generally suitable for *in situ* generation of these species in confined environments such as matrices (of course reagents that generate radicals by abstraction, such as the popular trialkyl tin hydrides, are also excluded from matrix isolation).

Two “chemical” strategies may be used to alleviate the cage problem: one consists in choosing precursors whose decomposition products include either a hydrogen atom, which can readily escape the matrix cage by diffusion, or a radical that will be unreactive toward the target radical. Cleaving C–H bonds photochemically is only possible in compounds which carry a chromophore that absorbs at (or above) the energy of the targeted bond. Unless far-UV light sources are available, this limits the strategy to precursors that produce resonance-stabilized radicals, such as benzyl or polyenyl radicals. On the other hand, it was found that atomic iodine or NO survive at least partially next to such reactive radicals as phenyl.⁴⁹ Thus, iodides and nitroso compounds should be considered as possible precursors for photolytic *in situ* generation of radicals, although they cannot be used generally, for example, to produce alkyl radicals.

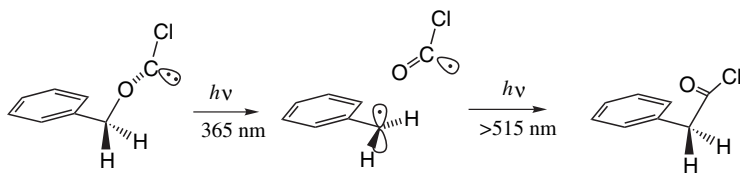
The second strategy is to design precursors that interpose one or two inert molecules between two fragments that are prone to recombination (see Scheme 17.3). For example, diacylperoxides undergo clean photocleavage into two radicals R^\bullet separated by a pair of CO_2 molecules that prevent at least some of the radicals enclosed in adjacent matrix cages from dimerizing.⁵⁰ The same strategy can also be employed to make matrix isolated biradicals (see, e.g., Chapter 16 in this volume). It was reported that a CO_2 and a CO molecule, such as they are produced on decomposition of acid anhydrides, $R-CO-O-CO-R$, may also suffice to keep two radicals at bay.⁵¹



Scheme 17.3

Occasionally, steric factors may prevent radicals from recombining. Thus we have recently found that the radicals $PhCH_2^\bullet + \bullet COCl$ which are formed on photolysis of oxychlorocarbene $PhCH_2OCCl$ (which is itself a reactive intermediate!) do not recombine spontaneously to form phenacetyl chloride $PhCH_2COCl$, presumably because the unpaired electron of the $OCCl$ radical “points” in the “wrong” direction to attack the benzyl radical. However, radical recombination *does* occur on annealing of the matrix, or on subsequent photoexcitation of the benzyl radical at >515 nm, which seems to provide the required energy its reorientation inside the rigid matrix cage (see Scheme 17.4).⁵²

Of course all of the above problems are avoided if a radical is generated *externally* and subsequently trapped in a matrix. If one wants to prepare a radical in a



Scheme 17.4

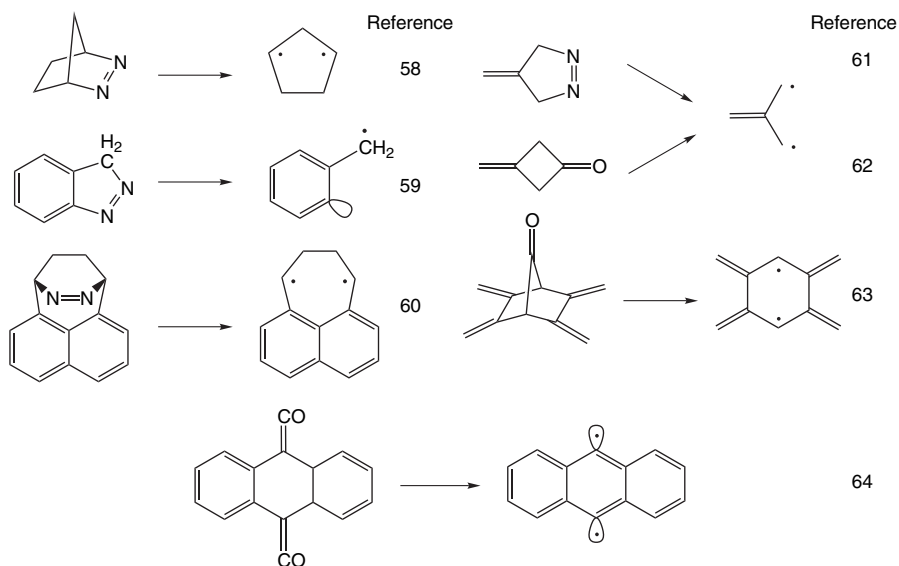
planned and controlled fashion, some form of *pyrolysis* is usually the method of choice. Most of the precursors that may be used for *in situ* generation of radicals described above are also useful sources of thermally created radicals. In addition, azo compounds ($R-N=N-R$) are convenient thermal precursors, and precursors with weak $C-C$ bonds, such as diphenylethane or 1,5-hexadiene, can also be employed as very clean sources of π -conjugated radicals. Also, bromides can be used instead of iodides, which are sometimes more difficult to synthesize.

In early studies, flash vacuum pyrolysis, a method that has proven very valuable in preparative studies of closed-shell compounds,⁵³ was regarded as the method of choice for the production of radicals for matrix isolation studies.⁵⁴ The disadvantage of this method, which is very well suited for preparative studies of closed-shell compounds, is that the reaction occurs on the walls of a hot tube whose surface may trap radicals (this problem may be alleviated by coating the inside of the tube with gold⁵⁵). Also, unless a very low vacuum can be maintained in the pyrolysis tube, collisions between radicals may lead to gas-phase dimerization.

All of these problems are overcome if the precursors are pyrolyzed in an inert host gas at high pressure, because under these conditions energy transfer occurs mostly by collisions with the host gas, and radical recombination is largely suppressed. Of course, a constant stream of hot gas at high pressure is incompatible with the requirements of matrix isolation, so the experiment has to be carried out in a *pulsed* fashion. Chen and co-workers^{16,56} were the first to propose what they called a “hyperthermal nozzle” for pulsed pyrolysis at very high temperatures, at that time for gas-phase studies. Several research groups have implemented variants of this design^{49,57} for work in matrix isolation and have used it successfully for a variety of studies.

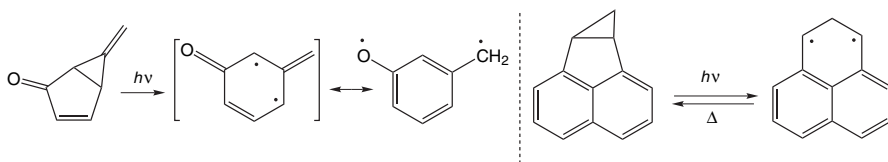
6.3. Biradicals

Whereas generation of monoradicals require cleavage of a *single* bond, formation of biradicals by fragmentation involves sequential or simultaneous cleavage of *two* bonds. If those two bonds involve the same moiety, one of the fragments is therefore a closed-shell species. By taking advantage of this fact, many matrix isolation studies on biradicals have employed precursors designed to yield these species on thermal and/or photochemical (*in situ*) extrusion of N_2 or CO . A few typical examples are given in Scheme 17.5.


Scheme 17.5

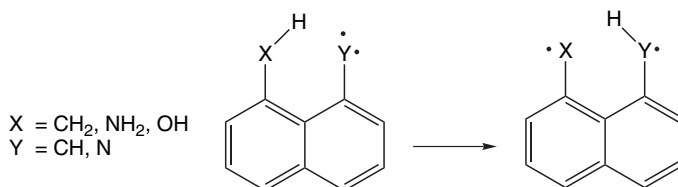
Of course, biradicals can also be generated by a sequence of two cleavage reactions such as described above for monoradicals, for example, from diiodides or bis(acylperoxides). Several examples of this strategy can be found in Chapter 16 in this volume.

In biradicals, where the two unpaired electrons can recombine to form a covalent bond, the resulting species may in turn serve as a potential precursor for the biradical. This only works in cases where the resulting biradical has a triplet ground state, which creates a spin barrier for the re-formation of the original bond. Two typical examples where this strategy succeeded are illustrated in Scheme 17.6.^{65,66}


Scheme 17.6

Finally, some diradicals can be made *in situ* by an internal hydrogen-transfer reaction from a suitable hydrogen donor to a carbene or nitrene. In benzene derivatives, this is a well-tested route to *o*-quinoid compounds, which are not biradicals, although a biradical valence structure probably makes a significant contribution to their electronic structure. However, if the donor and the carbene or nitrene are

attached at the 1 and 6 positions of a naphthyl moiety, then perinaphthadiyl diradicals result (see Scheme 17.7).^{67,68}



Scheme 17.7

The yield of triplet biradicals in all of the above processes is usually high enough to get very good ESR spectra (provided of course that the species has a triplet ground state, or that this state can be significantly populated from a singlet ground state at the temperature of the experiment). However, this says nothing about the relative or absolute yield of the target biradicals obtained from one or the other type of precursor. The samples studied by ESR spectroscopy may contain mainly ESR-silent byproducts that may predominate in UV-vis or IR absorption spectra. Several cases are known where ESR and UV-vis spectra gave conflicting evidence with regard to the identity of the species formed from a certain precursor.

An example is trimethylenemethane (TMM), one of the first hydrocarbon biradicals whose triplet ESR spectrum was recorded^{61,62} (cf. Chapter 5 in this volume), but which eluded 25 years of efforts (among others by the present author) to obtain its UV-vis or IR spectrum, because the predominant product of photolysis or pyrolysis of different precursors was invariably methylenecyclopropane (MCP). Eventually, Maier et al.⁶⁹ successfully generated a sufficient quantity of TMM, by irradiation of MCP in halogen-atom doped Xe matrices, to record the IR spectrum of this elusive compound.

An intriguing aspect of matrix isolated biradicals is that they can in some cases persist in two different spin states, which may even be interconverted photochemically or thermally. The reader is referred to Chapter 5 in this volume for a more detailed discussion of this phenomenon.

6.4. Radical Ions

Although radical ions may appear as somewhat exotic species to many physical organic chemists, they are pivotal reactive intermediates in all processes involving *single electron transfer*, which occur in many important reactions of biological (e.g., enzyme catalyzed oxidations) and technical relevance (e.g., photoinduced electron transfer, imaging). More recently, radical cations have also moved into the focus of astrochemistry, because they may account for many of the absorptions observed in the diffuse interstellar clouds. Therefore, assessing the identity, structure, and properties of radical ions is of great interest, and matrix isolation constitutes at least potentially an excellent tool for their investigation, because it allows one to leisurely study the properties of these highly reactive species.

Actually, the history of matrix isolation studies of radical ions is long and rich and has been reviewed repeatedly,^{26,28,70,71} but since most of these studies involve small molecules isolated in Ne matrices (where the interaction with charged species is minimal), not many of examples have found their way into the literature consulted by physical organic chemists. In these studies, radical ions were usually produced in open microwave or electric discharges, or by direct irradiation during deposition with far-UV light. More recently, several laboratories have succeeded in incorporating sufficient quantities of radical ions from mass selected ion beams into noble gas matrices to allow investigations by UV-vis and IR absorption spectroscopy.²⁸ In particular, Maier's group has applied this technique very successfully to study a variety of carbon chain molecules and ions by matrix isolation.⁷²

Although many highly interesting species can be generated by the above techniques, these methods are not suitable for systematic investigations of organic radical ions because they involve either direct interaction of the precursors with high energy radiation or, in the case of mass selected ion beams, a very high collision energy when the ion hits the matrix. These processes may lead to unwanted and often uncontrollable fragmentations or other chemistry.

On the other hand, in the 1960s Hamill⁷³ pioneered a technique for *radiolytic* production of radical ions in selected frozen solvents, which was further developed and applied to the study of a great variety of organic species by Shida.⁷⁴ Although the samples investigated by this method are exposed to very high-energy radiation (usually ⁶⁰Co γ -rays of > 1 MeV), the main result of this radiolysis is ionization of the frozen solvent that subsequently oxidizes the substrate (which itself is largely transparent to this radiation) to form its radical cation. If a halide, such as a Freon, is used as a solvent, then the ejected electron gets trapped by dissociative attachment. If MTHF, which is a very good hole trap, is used as a solvent, then the added substrate is often a better electron scavenger than the solvent, and thus radical anions can be formed.⁷

In the 1980s, the group of the present author applied this method to noble gas matrix isolation, with the hope of recording the IR spectra of organic radical cations. We took advantage of the fact that Ar has a very high cross-section for the bremsstrahlung emanating from a conventional X-ray tube fitted with a tungsten target, and Ar is thus very efficiently ionized by such X-radiolysis. Subsequently, the hole and the ejected electron travel through the matrix by resonant charge transfer (or in the form of polarons) until the hole gets captured by an added substrate with a lower oxidation potential than Ar (in solid Ar). If no extra measures are taken, most of the electrons get scavenged by some impurities such as CO₂ that are always present in matrices, but we found that much cleaner results are obtained when an organic halide (CH₂Cl₂ has proven very useful) is added as an electron scavenger in roughly equimolar amount to the substrate to be oxidized.

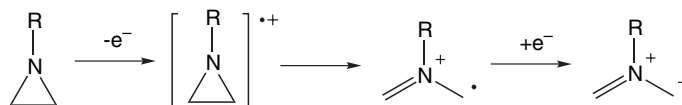
The above technique, which is very easy to implement (all that is needed besides the usual matrix isolation equipment is a conventional X-ray source for crystallography), was used first to record UV-vis spectra³⁷ and later IR spectra^{75,76} of numerous radical cations isolated in Ar matrices. The method seems to be quite generally applicable to any substrate that can be volatilized without decomposition.

A great advantage of the method is that the positive and negative charges reside in different cavities of the matrix, and therefore do not perturb each other.

Two main limitations have, however, become evident: the first is that molecules whose gas-phase ionization energy exceeds > 9.5 eV cannot be oxidized by ionized solid Ar. The reason for this limitation is unclear, because the process is exothermic (the ionization energy of solid Ar is 13.9 eV,⁷⁷ that of organic molecules in Ar is typically lowered by ~ 1 eV in solid Ar relative to the gas phase⁷⁸). Perhaps the localization of the spin and charge onto the substrate entails a Frank–Condon barrier that cannot easily be surmounted at 12 K.

The second limitation arises from the fact that the excess energy that is imparted onto the incipient substrate radical cations (which can be several eV!) cannot be efficiently dissipated in an Ar matrix, and is therefore temporarily available to drive low activation rearrangements or fragmentations. As a consequence, metastable primary radical cations, such as those of compounds containing, for example, diazo groups or small rings, often cannot be observed in Ar matrices. In these cases, recourse must be taken to frozen glasses where energy dissipation is much more efficient.

An interesting aspect of this method of preparing radical cations is that, as the substrate radical cations accumulate in the matrix, they begin to compete very successfully with the added halide for the electrons that are liberated during the radiolysis of the Ar. Usually, the only effect of this process is that the yield of radical cations tapers off after a while (usually at 10–15% of the neutral substrate) due to continuous reneutralization. However, if ionization is accompanied by some spontaneous rearrangement or fragmentation, then what gets neutralized is the rearranged species, or the fragment that carries the charge. This permits the accumulation of *neutral* reactive intermediates that may be difficult to generate by other means.⁷⁹ An illustrative example are azirines which undergo spontaneous ring opening to yield radical cations of azo methine ylids on ionization. Re-neutralization then leads to the neutral azomethine ylids that cannot be generated directly, for example, by photolysis of azirines, in quantity (see Scheme 17.8).⁸⁰



Scheme 17.8

So far, most of this discussion applies to the generation and study of *radical cations*. How about *radical anions*? These species are more difficult to generate in isolated form in cryogenic matrices because in solvents that do not significantly stabilize charged species (such as noble gases), isolated radical anions are prone to suffer detachment of the loosely bound extra electron, either spontaneously or under the impact of low-energy radiation. This situation contrasts with that encountered in solvents such as methyltetrahydrofuran, which can be routinely

used to generate and study radiolytically generated organic radical anions at 77 K.^{7,74}

Due to this limitation, the literature on matrix isolated radical anions is much less plentiful than that on radical cations. Several small radical anions were obtained more or less coincidentally as products of plasma reactions in discharges, or on vacuum ultraviolet (VUV) irradiation during sample deposition, but their identification was usually difficult due to the presence of numerous species with overlapping transitions. Of course the technique of mass selection in ion beams allows one to isolate negatively as well as positively charged species. Thus, Maier and co-workers⁸¹ fitted a source of negatively charged carbon chain radicals C_n^- (obtained by sputtering a graphite target with Cs^+) with a mass filter and interfaced the entire source to a 4 K matrix isolation apparatus. By virtue of their high electron affinities (~ 4 eV), these anions survived probing by UV/vis and IR absorption spectroscopy in Ne matrices, although they could be readily bleached by UV-photodetachment.⁷² The only systematic way to generate radical anions for matrix isolation studies is by capturing electrons liberated by photolysis of codeposited alkali atoms, a technique that was pioneered by Kasai.⁸² However, this technique has two disadvantages: First, in order to effect photoionization with visible light (UV light usually bleaches radical anions) the wave functions of the excited donor (alkali metal atom) and the acceptor must overlap to some degree. Therefore the resulting radical anions are not really isolated and their spectroscopic manifestations will be influenced by the nearby alkali cation. Second, matrix isolated alkali atoms show very strong absorptions throughout the visible spectrum,⁸³ which make it very difficult to probe radical anions in this spectral range. The pioneering studies of Kasai were done by ESR spectroscopy, which is not affected much by either of the above limitations.

Recently, the group of Salama has, however, begun to apply the above technique to the study of vibronic spectra of polyacenes that have the dual advantage that they have rather large electron affinities and that they absorb in the near-IR region where alkali atoms, in particular Na, do not absorb.^{83,84}

Finally, we wish to mention an attempt to create radical anions by X-irradiation of Ar matrices containing trialkylamines as codopants,⁸⁵ which release electrons on oxidation by ionized Ar (cf. Section 6.4). However, only small amounts of the targeted radical anions could be obtained by this technique.

6.5. Closed-Shell Ions

Closed-shell ions are among the most important intermediates in solution chemistry, and no treatise on reactive intermediates (including the present one) would be complete without extensive sections on carbocations and carbanions, if not also on heteroanalogues of the above species. Nevertheless, closed-shell ions are conspicuously absent from matrix isolation studies, apart from a few cases where such species were coincidentally formed in discharges, or where charged species were deliberately "isolated" by mass spectrometry (cf. Section 6.4). The reason for

this is that closed-shell ions are usually generated in *bimolecular* reactions, typically with Brønsted or Lewis acids or bases, that cannot easily be realized under the conditions of matrix isolation.

However, there are some exceptions. One of them is the possibility of (*photo*)-*protonation* or *deprotonation*. If a matrix is doped with sufficient amounts of a proton donor or acceptor, chances are that the substrate will give up or accept a proton already on cocondensation or on subsequent photoexcitation. In fact, the higher noble gases (Ar, Kr, Xe) are themselves good proton acceptors, forming $(\text{NG}_n \cdot \text{H})^+$ complexes that can be identified by their characteristic IR vibrations.⁸⁶ This feature allows occasionally to observe radicals formed by deprotonation of radical cations formed in noble gas matrices, for example, benzyl radical from ionized toluene.⁸⁷ However, we know of no examples where a carbanion was formed by deprotonation in matrices.

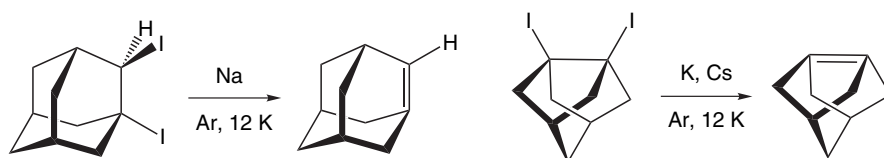
On the other hand, it is known that carbenes and nitrenes can be protonated to yield carbocations^{88,89} or nitrenium ions, respectively.^{90,91} Thus, if carbenes or nitrenes are generated in the presence of a protic acid in a matrix, at least some of them should be protonated. This concept has recently been tested in the case of arylnitrenes whereby substantial quantities of nitrenium cations were identified when the corresponding azides were photolyzed in Ar matrices containing 10–30% HCl.⁹² However, the species formed in this way arise of course in the form of *ion pairs*, and therefore one cannot speak of truly matrix-isolated cations.

Another possibility to generate closed-shell cations in matrices is by ionization of the corresponding radicals, for example, by VUV photolysis in Ne or by X-radiolysis in Ar (cf. Section 6.4 on radical ions). What is required for such experiments is a clean source of radicals (to avoid the occurrence of multiple products) and a source of ionizing radiation. The only example where this experimental ansatz, which can potentially lead to truly matrix isolated closed-shell cations, has been put into practice was recently provided by Winkler and Sander. Among the compounds that they obtained on irradiation of iodobenzene with the 105–107-nm light from an Ar discharge lamp during deposition, they were able to identify the phenyl cation that was doubtlessly formed by ionization of the phenyl radical, which was also present in the matrix. However, a generalization of this procedure would require a separation of the radical forming from the ionization step, such that difference spectra for the latter step, which contain only signals from ionized products, could be obtained. Also, it would be desirable to generate radicals in the absence of nearby electron scavengers (such as iodine atoms) in order to avoid formation of ion pairs.

6.6. Other Reactive Intermediates

Of course, matrix isolation studies are not limited to the classes of reactive intermediates discussed in the above five sections. There are many other types of highly reactive species that can be stabilized (and were often observed for the first time) in cryogenic matrices. Only a comprehensive review could do justice to all those efforts, but this effort is beyond the scope of this chapter. So, we will limit ourselves to a few typical cases.

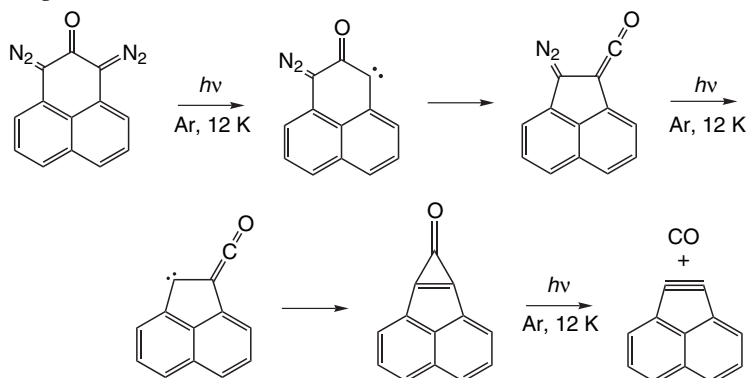
One highly reactive structural motif that has found great attention are bent triple bonds (cycloalkynes or -arynes), and twisted or strongly pyramidalized double bonds, such as anti-Bredt olefins or unsaturated cage compounds. Several such species have been immobilized and identified in cryogenic matrices (for *o*-benzynes, the reader is referred to Chapter 16 in this volume). In solution, such compounds are often generated by dehalogenation (e.g., with Na amalgam) or dehydrohalogenation (with strong bases). Dehalogenations can also be carried out by co-condensation of dihalides (usually diiodides) with alkali atoms.³³ This strategy has been followed to generate such species as the highly twisted adamantene⁹³ or the strongly pyramidalized tricyclo[3.3.1.0^{3,7}]nonene⁹⁴ shown in Scheme 17.9.



Scheme 17.9

Dehydrohalogenations (elimination of HX) can in turn be effected by passing the halide over a solid base such as vacuum-dried hot KOH⁹⁵ or *t*-BuOK⁹⁶ adsorbed on some carrier material. Recently, Billups et al.⁹⁷ showed that elimination of Me₃SiBr may even be effected at room temperature over solid CsF. Several very interesting strained alkenes have been generated by such techniques, but although these techniques would lend themselves very well for interfacing to matrix isolation we know of no example where this has been achieved.

In situ generation of strained alkenes or alkynes requires photoelimination of a leaving group toward which the targeted product is unreactive. Thus, cycloalkynes may be generated by elimination of CO from cyclopropanones, but these must in turn be generated *in situ* (e.g., from diazoketones). The generation of acenaphthyne⁹⁸ (Scheme 17.10) may serve as an illustration of this procedure that did, however, not work for the parent cyclopentyne, a compound that still awaits spectroscopic characterization.



Scheme 17.10

Note that not all cyclopropanones eliminate CO photochemically. Thus, the first cyclohexynes had to be generated by *pyrolysis* of the precursor cyclopropanone.^{99,100}

A very particular strained alkene, cyclobutadiene (CB), has a rich and instructive history that has been reviewed repeatedly.¹⁰¹⁻¹⁰³ As matrix isolation work by several groups played a pivotal role, and as some important lessons can be learned from this story, it merits closer attention in the present context. In trapping studies conducted in the 1960s, CB displayed a Janus-faced pattern of reactivity in that it underwent cycloaddition reactions, which are typical for dienes, but it also proved to be extremely reactive toward molecular oxygen, halogen atoms, methyl- and allyl radicals, as is typical for triplet biradicals. Much of the discussion centered therefore on the disposition of the singlet and triplet potential energy surfaces as depicted in Figure 17.6.

All calculations agreed that triplet CB would be square, whereas singlet CB would have a rectangular geometry, but the calculations disagreed in their predictions with regard to the relative energies of the two states (situations *a*, *b*, and *c* in Fig. 17.6), especially with respect to the ground state multiplicity (and hence the structure) of CB. As it was unclear in what way substituents would influence this situation, studies on the parent compound were called for to settle this question, and these could only be done in the gas phase or in matrices.

By 1973, the groups of Chapman et al.¹⁰⁴ and Krantz et al.¹⁰⁵ had obtained IR spectra of parent CB as well as of its mono- and dideuterated derivatives, which

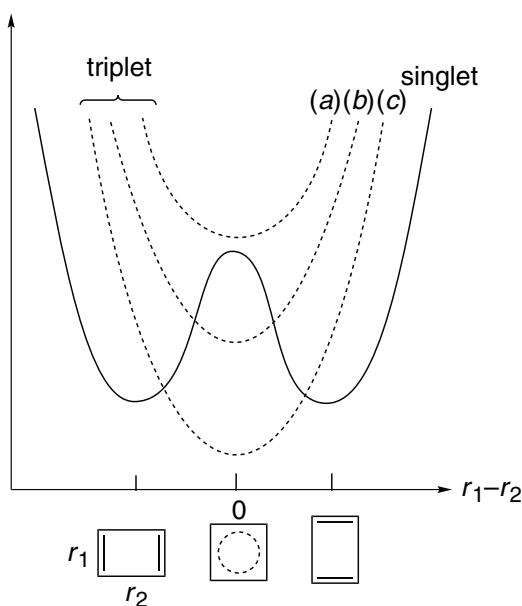
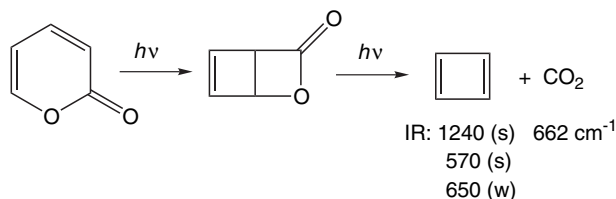


Figure 17.6

they generated from photo- α -pyrone (Corey's lactone), created *in situ* from α -pyrone. The spectra of CB- h_4 obtained by the two groups showed two strong bands at ~ 1240 and 570 cm^{-1} and a weaker one at $\sim 650\text{ cm}^{-1}$, close to the bending vibration of the coproduct, CO_2 , at 662 cm^{-1} (Scheme 17.11).



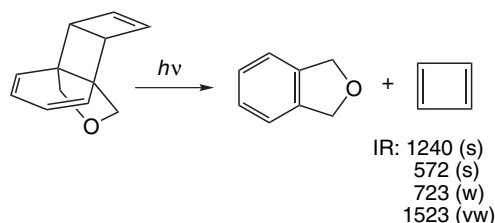
Scheme 17.11

Group theory predicts that if parent CB is square, it should show *four* IR active fundamentals (of which one was a degenerate C—H stretch expected to be of very weak intensity). On the other hand, if parent CB were rectangular, it should show *seven* IR active fundamentals of which two are weak C—H stretches. Since only *three* (rather than five) bands were observed in the IR spectrum of CB below 2000 cm^{-1} , Krantz and Newton concluded that CB must be square. They supported this conclusion with a force-field calculation, based on a square geometry, that reproduced the observed frequencies, including those of CB- d_1 , to within a few wavenumbers.¹⁰⁵ On the other hand, Chapman conjectured that the absence of evidence for two different vicinally dideuterated CB- d_2 (which would be expected for rectangular CB- d_2 and can exist as a 1,2- and 1,4-isomer) agrees also with a square structure.

The problem with the above assignment was that theory predicted unanimously that square CB should have a triplet ground state. However, all attempts to record an ESR spectrum of this putative triplet diradical under various conditions failed. Furthermore, theory also predicted that square triplet CB should show a strong transition at $\sim 370\text{ nm}$,¹⁰⁶ whereas rectangular singlet CB should be transparent down to 200 nm .^{107,108} Although the exact position of an absorption that should be ascribed to CB was a matter of some debate, agreement prevailed with regard to the fact that it was weak and not above 300 nm , which posed an additional problem with respect to the assignment to square triplet CB.

All of this led the groups of Maier et al.¹⁰⁹ and Masamune et al.¹¹⁰ to reinvestigate the IR spectrum of CB, in search of possible bands that might have escaped detection in the experiments of Chapman and Krantz. To this end, they employed different precursors of which the formal adduct of CB with phthalan proved to be the optimally suited.

To their great surprise, both groups started by finding *fewer* bands than had been found in the studies of Chapman and Krantz! In particular, the strong 660-cm^{-1} band appeared to be linked to the presence of CO_2 . Maier concluded that it must have been due to a splitting of the degenerate bending vibration of CO_2 due to complexation with CB.¹⁰⁹ This conclusion was confirmed a year later through ^{13}C labeling experiments.¹¹¹



Scheme 17.12

However, this finding did not solve the problem at hand. In fact, it took Masamune et al.^{112,113} several years, involving studies with differently deuterated precursors, to finally confirm the presence of two additional weak bands at 723 and 1523 cm^{-1} (1456 and 609 cm^{-1} in CB-d_4), which they could unambiguously assign to CB (Scheme 17.12). With the proven presence of *four* IR bands below 2000 cm^{-1} the hypothesis that CB is square was definitely refuted.^{114a}

The reason why we relate this particular story in some detail is because two very important lessons can be learned from it: first, *drawing conclusions on the basis of missing evidence is often misleading*.^{114b} Second, it is always highly desirable to generate a reactive intermediate independently *from different precursors*. Only spectral features that appear in experiments involving at least two independent pathways of formation of a targeted species can be assigned with confidence to that species. If chemically different precursors are not available, one should at least try to play with isotopic substitution and make sure that the shifts of vibrational bands are in accord with expectations for the targeted species.

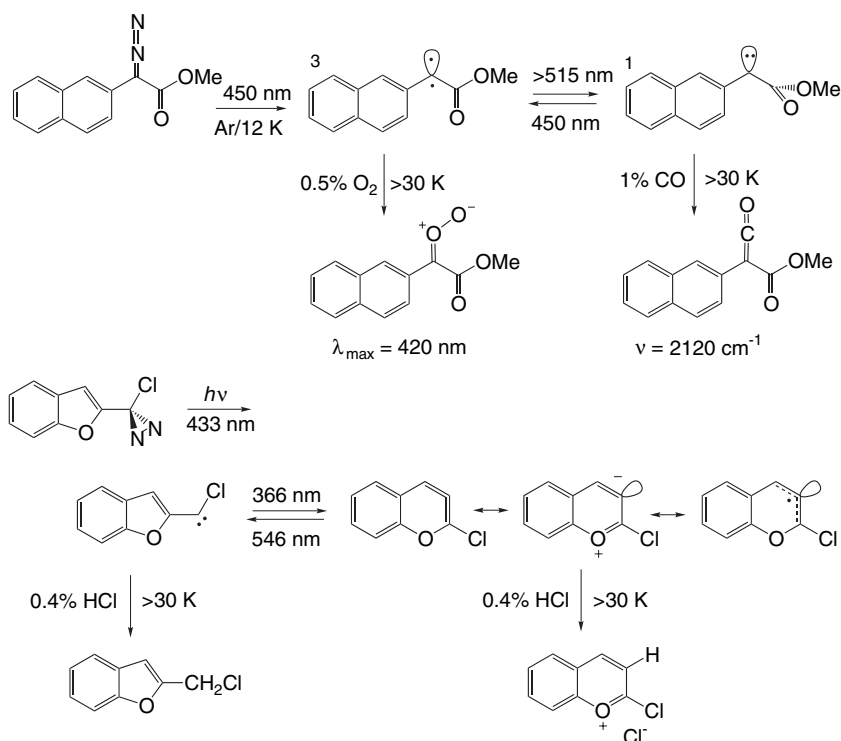
7. PROBING MATRIX-ISOLATED REACTIVE INTERMEDIATES

7.1. General Remarks

With few exceptions, all investigations of matrix-isolated reactive intermediates are done by *absorption spectroscopy*, in the UV–vis and/or in the IR spectral range, or, in the case of open-shell species, by *ESR*. Occasionally, one also finds studies where emission or Raman scattering of reactive intermediates is probed in matrices, but these studies are few and far between, so we will focus in this section on the first group of techniques that can be easily implemented with commercially available equipment.

A first point to consider is that thermal or photochemical decomposition of a precursor often does not lead to a single product, due to parallel or consecutive secondary reactions. Since absorption spectroscopy invariably probes all components of a mixture, the problem of how to distinguish between these components may arise in the context of studies on reactive intermediates. This problem can be

addressed by searching conditions under which the concentration of only one or the other compound change, for example, by taking recourse to *trapping reactions* (Scheme 17.13). Thus, triplet carbenes are very reactive toward molecular oxygen



Scheme 17.13

and slight annealing of matrices doped with 1–2% O₂ usually leads to the rapid disappearance of triplet carbenes and the formation of carbonyl oxides,¹¹⁵ which distinguish themselves by strong, broad UV bands peaking at 420–450 nm. On the other hand, singlet carbenes react readily with CO to yield ketenes that can easily be recognized by their strong IR peaks at ~2120 cm⁻¹. Singlet carbenes, nitrenes, and strained olefins can also be trapped in matrices by HCl, which leads either to protonation or to addition of HCl. Some representative examples of this are given in the above Scheme 17.12.^{116,117}

Another strategy consists in irradiating a sample at judiciously selected wavelengths to effect *selective bleaching* of one or another component of a mixture. Thereby, it is usually advisable to start by irradiating at the longest wavelength where the targeted product mixture absorbs, in order to avoid simultaneous bleaching of several compounds or the establishment of photostationary equilibria. Unfortunately, irradiation into the first absorption band does not always provide sufficient

energy to effect a photorearrangement or photocleavage reaction, and then one must move to shorter wavelengths which, of course, increases the risk that other components are bleached at the same time. However, by using different cutoff and interference filters, it is often possible to find a wavelength where at least one component is bleached much more efficiently than another, which allows the IR or UV-vis absorption bands of the two to be distinguished by their different “photo-kinetic” behavior.

Such photochemical experiments have the additional benefit that they may lead to the discovery of (unexpected) new species that can be just as interesting as the originally targeted reactive intermediate. For example, attempts to selectively bleach the triplet naphthyl carbomethoxy carbene shown in the Scheme 17.13 in view of its spectroscopic identification led to the serendipitous finding that the corresponding singlet carbene is also stable in an Ar matrix at 12 K, that is, the discovery of one of the rare cases of spin isomerism.¹¹⁶ Similarly, Sheridan and co-workers^{117,118} found recently that bleaching of 2-benzoylfurylchlorocarbenes (also shown in Scheme 17.13) leads to an entirely novel type of reactive intermediates, didehydropyrans, which have an interesting electronic structure.

Irrespective of how a targeted component of a mixture is affected, it is often easier to discern spectral changes by looking at *difference spectra*, that is, the results of subtraction of a spectrum taken after annealing or bleaching from that taken before. However, if meaningful difference spectra are to be obtained it is crucial to assure a highly *reproducible sample positioning* so that the beam of the spectrometer always probes the exact same part of the matrix. A reproducible sample positioning can be achieved by means of a template whose dimensions fit the bottom of the vacuum shroud and which is mounted inside the spectrometer’s sample chamber.

One is in an even better situation with regard to the identification of a reactive intermediate when one can examine *pairs* of difference spectra for the formation and the disappearance of a compound, because one can then readily discern the *mirror-image patterns* that must belong to the targeted species from other spectral changes that may accompany one or the other of these processes. Examples for this will be given in Sections 7.2–7.4 on IR and UV-vis spectroscopy.

7.2. Infrared Spectroscopy: Experiment

Infrared spectroscopy is by far the most popular tool for the investigation of matrix-isolated species. By virtue of the suppression of most rotations in solid matrices, IR spectra recorded under these conditions typically show patterns of very narrow peaks, compared to spectra obtained under normal laboratory conditions (solution, Nujol, or KBr pellets), where bands due to different vibrations often overlap to the extent that they cannot be separated. As a consequence, matrix isolation IR spectra are—at least potentially—are a very rich source of information on the species under investigation. Whether and how all this information can be used depends on the ability to assign the spectra, a subject to which we will return below.

However, when doing matrix isolation IR spectroscopy one should also be aware of some special features of this technique, and of some problems that one needs to address in order to be successful. One of these features is the so-called *site effect* that may lead to the splitting of bands that belong to a single normal mode. Site effects are a very well known phenomenon in the field of spectral hole burning or single molecule spectroscopy in solid media¹¹⁹ (indeed they make it possible to observe single molecules in many cases). Such site effects result from the fact that a rigid host material may accommodate a guest molecule in different local environments (sites) where these molecules may experience slightly different external fields or geometrical constraints. Consequently, the frequencies of certain normal modes may be shifted, either through the influence of the varying external field on the electronic structure of a host molecule, or through an effective increase in a force constant when the atoms have to work against the rigid environment along some normal mode. Depending on the type and size of the molecule and on the host material, this can lead to multiple sharp lines or to a general broadening of the IR absorptions.

The extent to which site effects manifest themselves in the spectra depends also on the way a matrix is made. It has been reported that pulsed deposition leads to a simpler spectral site structure and sharper lines than slow, continuous deposition. But then this depends on the backing pressure and pulse duration, as well as on the temperature of the matrix gas and the speed with which extra gas is removed, so no general rules can be given. Every practitioner of matrix isolation has to find a combination of these above variables that leads to the best spectra under their laboratory conditions. The search for these conditions should, however, not be guided by purely aesthetic spectral criteria, but by the need to acquire a maximum of useful information with minimal effort.

In practice, one finds that site effects often affect high-frequency framework or functional group vibrations that occur in the 1700–2300-cm⁻¹ range most pronouncedly. Everyone who has worked, for example, with heterocumulenes, diazo compounds, or azides, is familiar with the fact that the very intense asymmetric stretching vibrations that are associated with such groups often appear in the form of multiple, sometimes overlapping peaks that may extend over a region of 50 cm⁻¹ or more. Since all these peaks disappear simultaneously on photolysis, they must belong to the same species. To our best knowledge, the exact origin of these very strong site effects in the case of heterocumulenes is unknown, but they usually pose no assignment problems because no other vibrations occur in this spectral region.

When *pairs* of lines of different intensity occur in a region where only a single one is expected on the basis of normal mode calculations (cf. below), these need not indicate a site splitting, but are often indicative of *Fermi-resonances*, that is, a (near) coincidence of an IR active fundamental with a combination band that “borrows” intensity from the former. Such phenomena can often only be detected by virtue of the high resolution that is available in matrix isolation IR spectroscopy.

As mentioned above, it is often advantageous to look at *difference spectra*, and this is especially true in matrix isolation IR spectroscopy, because, due to the

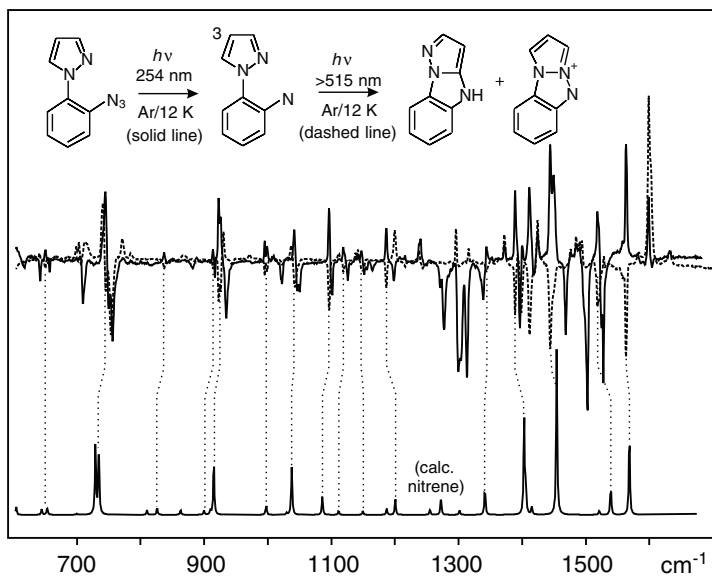


Figure 17.7

sharpness of bands, overlap between spectra of different compounds is often minimal. Fortunately, with the advent of interferometry, which eliminates the problem of hysteresis, precise wavenumber reproducibility, which, of course, is a prerequisite for obtaining meaningful difference spectra, is no longer a problem. Furthermore, the spectra automatically are present in digital form, which makes arithmetic operations trivial.

The case of pyrazolo-phenylnitrene (formed from the corresponding azide, solid line, and bleached selectively to yield a pyrazoloindole shown in Fig. 17.7) may serve as an illustration of this feature, which becomes even more evident when color is used. The trace shown at the bottom of this figure leads into the problem of spectroscopic assignments discussed in the Section 7.3.

7.3. Infrared Spectroscopy: Modeling

Up until about 1990, the main use of matrix isolation IR spectroscopy in connection with research on reactive intermediates was in the detection of signpost bands that allowed the detection and unambiguous assignment of certain functional groups. In many cases, where other spectroscopic evidence was lacking or inconclusive, such data were of course highly significant as a basis for mechanistic conclusions.

For example, the ring expansion reactions undergone by phenylnitrene and phenylcarbene manifested themselves for the first time by conspicuous IR bands at 1895 or 1815 cm^{-1} that were observed after photolysis of matrix-isolated phenyl

azide¹²⁰ or phenyldiazomethane, respectively¹²¹ and which Chapman and co-workers¹²² assigned to the asymmetric stretching vibration of the cyclic allenes, (aza)cycloheptatetraene. Often, however, it was found necessary to generate an intermediate independently from several precursors, or to take recourse to isotopomers to substantiate such assignments.

Unfortunately, most of the structural information of IR spectra is contained in the often very crowded region of 500–1600 cm^{-1} , which was hardly exploited for diagnostic purposes except in the case of very small molecules with few vibrations, or for pattern matching of spectra of reactive intermediates obtained independently from different precursors. The reason for this was that the prediction of IR spectra was only possible on the basis of empirical valence force fields, and the unusual bonding situations that prevail in many reactive intermediates made it difficult to model the force fields of such species on the basis of force constants obtained from stable molecules.

On the other hand, quantum chemistry was of limited help, although techniques to compute force fields from second derivatives became widely available in the 1980s. However, the force constants computed at the Hartree–Fock level generally proved to be too inaccurate to permit a reliable modeling of experimental spectra. The situation improved a bit when the effects of dynamic correlation were included, usually at the MP2 level (for details of the methods discussed in this section, see Chapter 22 in this volume). However, especially the off-diagonal elements that describe the mixing of valence deformations were still often of the wrong magnitude (or even of the wrong sign!), which led to unreliable predictions of normal modes and their frequencies. These shortcomings could be improved upon by a judicious method of scaling that was proposed by Pulay et al.¹²³ in 1983, but in order to work reliably, this scaling required the correct assignment of vibrational spectra obtained from several isotopomers. Although this method was occasionally applied to reactive intermediates,¹²⁴ it never gained much popularity in this field.

This situation changed drastically when it was discovered in the 1990s that *density functional* (DF) methods do a much better job of modeling force fields than (affordable) wave function based methods. Already within the local density approximation (LDA) of DF theory, vibrational frequencies were predicted with similar accuracy as at the MP2 level,^{125,126} and the agreement between calculated and experimental vibrational spectra became notably better when gradient-corrected functionals such as BP86 or BLYP were employed. In the mid-1990s, several studies were undertaken to assess the performance of different exchange and correlation functionals for predicting vibrational spectra.

Of these studies, we only wish to mention the seminal 1996 work of Scott and Radom¹²⁷ who investigated the performance of a variety of gradient-corrected and hybrid functionals (BLYP, BP86, B3LYP, B3P86 and P3PW91) with the 6-31G* basis set for predicting over one thousand vibrational frequencies from a large suite of test molecules. By least-squares fitting, they also derived scaling factors for each method that bring the predicted (harmonic) vibrational frequencies into optimal agreement with experimental ones. Thereby, they found that frequencies calculated by BLYP or BP86 require hardly any scaling, but are in slightly worse overall

agreement with experimental frequencies than those computed with the B3 hybrid exchange functional. Overall the best combination of functionals proved to be B3PW91 with a root-mean square (rms) deviation over the entire test set of 34 cm^{-1} and only 4% of frequencies that deviate by $>10\%$, all after scaling all frequencies by 0.9573. A close runner-up was B3LYP with the same rms deviation, but 6% of outliers, after scaling by 0.9614. Both DFT methods were much better than MP2/6-31G* (rms = 63 cm^{-1} , 10% outliers) and the much more expensive QCISD method (rms = 37 cm^{-1} , 6% outliers). Another very important finding of this study was that it usually does not pay to go to larger basis sets or finer quadrature grids, which is good news in terms of computational economy.

Thus it has now become possible for anyone with access to a modern PC to compute full vibrational spectra of any species that represents a minimum on its potential energy surface with sufficient accuracy to compare them directly with experimental ones. The *intensities* of IR transitions which are proportional to the changes of the dipole moment along the different normal coordinates are also an important element in this comparison. Although even relative intensities cannot be computed with similar accuracy as frequencies can, the assignment of an experimental spectrum to a certain molecule requires that no IR bands that are calculated to have high intensities are missing from the experimental spectrum, and that this spectrum does in turn not contain intense bands that are absent from the simulated spectrum. To summarize, there must be an evident and consistent relationship between the pattern of observed and the pattern of calculated IR bands for a structural assignment to be valid. It is very important to remember this because the temptation to succumb to a degree of wishful thinking in the process of pattern matching should not be neglected.

Amidst all the enthusiasm about this versatile new tool that quantum chemistry has put at the hands of practioners of IR spectroscopy in matrices, one should not forget its limitations. First, a valid prediction can only come from a calculation based on a correct structure. In the case of reactive intermediates, this is not always as evident as one might wish. A famous example is given in Chapter 16 in this volume: Much of the recent discussion on the correct assignment of the IR spectrum of *m*-benzynes was caused by the fact that different theoretical methods predict different structures, with more or less bonding between the radical centers, for this species. The DFT methods appear to overestimate this bonding, and hence are unsuitable for the prediction of the IR spectrum of *m*-benzynes.

A second instructive example that cautions us to watch out not only for molecular but also for the electronic structural features of species whose IR spectra we wish to assign comes from the recent work of Sheridan and Nikitina¹¹⁸ on didehydrobenzoxazine, which they were able to generate from an acetylenic quinonimine: A normal (spin restricted) B3LYP calculation of this species yielded an IR spectrum that showed "only marginal similarity" to the experimental spectrum. However, on removing the requirement that pairs of electrons occupy the same spatial molecular orbitals, the calculation relaxed to a broken-spin structure describing a mixed singlet-triplet diradicaloid state that led to a satisfactory IR prediction.

Another limitation is inherent to the harmonic approximation on which standard quantum mechanical force-field calculations are invariably based. Due to a fortuitous (but surprisingly systematic) cancellation of errors, the harmonic frequencies calculated by modern density functional methods often match very well with the experimental ones, in spite of the fact that the latter involve necessarily more or less anharmonic potentials. Thus one is tempted to forget that the harmonic approximation can become perilous when strong anharmonicity prevails along one or another molecular deformation coordinate.

An example of an otherwise fairly “normal” reactive intermediate where the harmonic approximation fails is phenylcarbene (see Fig. 17.8): Although the match between calculated and observed IR bands is quite satisfactory across most of the spectrum, it breaks down completely in the region of 750–950 cm^{-1} , where there is not even a remote similarity between the pattern of three bands predicted by B3LYP calculations (dashed line) and those found experimentally (solid line, downward pointing peaks).

An analysis of the reasons for this discrepancy⁴⁵ revealed that the three normal modes that are excited in this frequency range comprise to varying degrees the Ph–C–H bending deformation which, by explicit calculation of the potential energy surface, turned out to be rather strongly anharmonic. A selective reduction of the Ph–C–H bending force constant in a Pulay-style scaled force-field calculation led to a prediction that is at least qualitatively in better accord than the unscaled B3LYP prediction in this frequency range (see inset in Fig. 17.8). However, accommodating anharmonicities of selected deformations in this way cannot be regarded

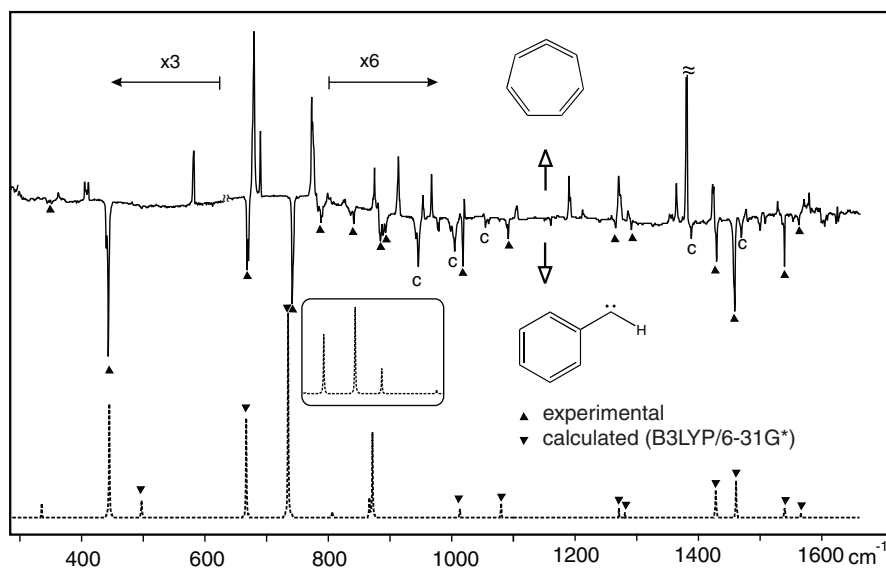


Figure 17.8

as a valid remedy, because anharmonicity affects also the mixing of valence deformations that interact to give normal modes.

7.4. Ultraviolet–Visible Spectroscopy: Experiment

Although IR spectra contain inherently more information than UV–vis absorption spectra, the information contained in the latter is often more directly useful. In particular, selective bleaching experiments require a knowledge of the electronic absorption spectra, and these spectra may also give valuable hints with regard to the presence of possible products. For example, triplet aryl carbenes are readily recognized by their characteristic sharp bands in the 400–500-nm range,⁴⁵ and polyenyl radicals or polyene radical cations by their pattern of a weak but sharp vis–NIR band accompanied by an intense near-UV transition.¹²⁸ Therefore UV–vis spectra should be taken routinely also in experiment targeted at recording IR spectra.

Fortunately, this requires no additional investment (apart from a UV–vis spectrometer that is, however, available anyway in most laboratories), because highly polished salt (KBr or CsI) windows are sufficiently transparent down to 200 nm so that high-quality UV–vis spectra can be obtained with the exact same sample configuration as is used for IR absorption spectroscopy. As in IR spectroscopy, it is often useful to look at difference spectra, but as bands due to different compounds have much more of a tendency to overlap in this case, which may lead to distortions in the difference spectra, one has to be cautious in assigning band maxima from difference spectra.

Although *site effects* are not as prevalent in UV–vis absorption as they are in IR spectra, they do exist and manifest themselves sometimes very clearly in band systems that comprise sharp peaks. An example is the radical cation of all-*trans*-octatetraene whose first absorption band consists of multiple peaks that can be selectively bleached by highly monochromatic light.¹²⁹ The site structure can become more evident in laser-induced fluorescence, where excitation of individual sites is possible down to the level of single molecules in favorable cases, but a discussion of this fascinating phenomenon is beyond the scope of this chapter.

7.5. Ultraviolet–Visible Spectroscopy: Modeling

Unfortunately, the situation with respect to the modeling of electronic absorption (or emission) spectra in view of their use in assignments of reactive intermediates is not nearly as comfortable as in the case of vibrational spectroscopy. No universal and affordable “magic bullet” such as the B3LYP/6-31G* method has been found, and thus reliable calculations of excited-state energies and transition moments (i.e., the constituents of electronic absorption spectra) require usually more effort and circumspection. However, that should not discourage interested users from venturing into this very exciting (albeit a bit slippery) field of computational chemistry, and these users may take comfort from the fact that many successes have been achieved, and that modeling of electronic absorption spectra has permitted us to

clarify complicated mechanistic schemes in cases where IR spectroscopy could not be applied for one reason or another.

The difficulties are mainly caused by two problems: (1) the fact that even a qualitatively correct description of excited states often requires *multiconfigurational wave functions*; and (2) that dynamic electron correlation effects in excited states are often significantly greater than in the electronic ground states of molecules, and may also vary greatly between different excited states. For explanations of the concepts invoked in this section, see Section 3.2.3 of Chapter 22 in this volume. Therefore, an accurate modeling of electronic spectra requires methods that account for both effects simultaneously.

The multiconfigurational problem can be readily handled by a CI (configuration interaction) calculation limited to a restricted number of “active” orbitals and electrons and/or to a certain excitation level (simultaneous excitation of one, two, or three electrons). However, such calculations do not account sufficiently for dynamic electron correlation, which therefore has to be introduced “on top.” Over the course of time, different strategies have been elaborated to achieve this. The simplest and most straightforward one is to introduce *parameters* into a model and to calibrate those on a test set of well-known and correctly assigned electronic transitions. This approach, which was implemented back in the 1950s at the Hückel level, and was subsequently applied to π - and later to all-valence-SCF-CI semiempirical methods, has a long and successful history. However, the application of these methods to species with unusual bonding situations (such as many reactive intermediates) is problematic because such compounds were usually not included in the parametrization. Nevertheless, methods like the popular INDO/S-CI model of Zerner and Ridley¹³⁰ have been and continue to be applied very successfully to the modeling of the electronic spectra of reactive intermediates.^{116,131} Apart from the fact that these semiempirical methods are inexpensive in terms of computational resources, another advantage is that these are very transparent because the excited configurations are built from a set of Hartree-Fock MOs.

Accounting for dynamic correlation effects at the *ab initio* level requires that a multiconfigurational calculation be supplemented by a large CI (MR-CI) or by a perturbative treatment, for example, by the MP2 or coupled cluster methods described in Section 3.2.3.2 of Chapter 22 in this volume. The most widely applied of these is the CASPT2 method that was developed by Roos and co-workers¹³² and is implemented in the MOLCAS suite of programs.¹³³ There an MP2-type calculation is carried out on the basis of a zero-order CAS (complete active space) self-consistent field (SCF) wave function (cf. section 3.2.3.3 of Chapter 22 in this volume). Conceptually, this is a very elegant approach, but in practice CASPT2 calculations on excited states are often fraught with problems. The reason is that excitations from or into MOs *outside* the active space, which are generated in the MP2 step, may be nearly degenerate with excitations *within* the active space, which leads to a breakdown of the perturbative *ansatz*. For small molecules, this problem can sometimes be overcome by increasing the active space, but for large molecules this is often impossible because the size of a CASSCF calculation scales factorially with the number of MOs in the active space. Then one is forced to take

recourse to level-shifting techniques that lack a solid theoretical foundation and may lead to artifacts. Nevertheless, if applied with due circumspection, CASPT2 is a very reliable method and has been applied successfully to the modeling of electronic spectra of a wide variety of compounds, including many matrix-isolated reactive intermediates in the author's laboratory.^{8,134–142}

An entirely different approach to ab initio calculations of excited states is to look at the *response* of the ground-state electron distribution to oscillating electric fields of different frequencies. If the frequency of such an oscillation is in resonance with an electronic excitation, then the polarizability will increase discontinuously, that is, the *frequency-dependent polarizability* will show a *pole* whose intensity is proportional to the electronic transition moment. To probe this, one must solve a *time-dependent* Schrödinger equation. The corresponding formalism, which allows one also to calculate states where electrons are detached or added, was developed a long time ago for Hartree–Fock theory, but the lack of dynamic correlation at this level made it impossible to obtain accurate results. This situation changed when the above *ansatz* was carried over to density functional theory where dynamic correlation is accounted for by means of the exchange and correlation functionals.¹⁴³ After the implementation of this so-called time-dependent DFT (TD–DFT) method into the Gaussian series of programs,¹⁴⁴ the application of this method has gained a measure of popularity in recent years, mainly because it is considerably more economical in terms of computational and human resources than the above CASPT2 method. Since the excited-state electron density is modeled within the framework of a singles-CI, the results of TD–DFT calculations also lend themselves to a transparent interpretation in terms of electronic configurations. The TD–DFT theory also has recently been applied successfully to matrix-isolated reactive intermediates,^{142,145,146} but the experiences made in our laboratory are mixed and the jury is perhaps still out on how reliable this promising new method really is.

Finally, we wish to mention that Grimme et al.¹⁴⁷ proposed a very economical multireference (MR) method based on the MOs obtained by DFT calculations (DFT–MRCI), whereby an overaccount for dynamic correlation is prevented by introducing empirical parameters. Although the introduction of these parameters gives this method a semiempirical flavor, its quantitative accuracy in the prediction of spectra appears to be comparable to that of CASPT2, at a fraction of the expense of computational and human effort.¹⁴² In fact, DFT–MRCI has even yielded predictions in excellent agreement with experiment even in a recent case where CASPT2 failed entirely.¹⁴⁸

8. CONCLUSION AND OUTLOOK

Research on reactive intermediates can be carried out by different approaches and techniques that are often complementary. The first, and the oldest of these approaches, involves *product studies* where conclusions about the properties of a reactive intermediate are drawn from the chemistry it undergoes. Translated into forensic terms, such studies amount to an investigation of the scene and the victims

of the crime after the crime has been committed. Much closer to the action is *time-resolved* spectroscopy, which looks at the appearance or disappearance of some manifestation of the reactive intermediate or one of its “victims” (i.e., the proverbial “smoking gun”). Although, if judiciously designed and interpreted, both of the above methods make it possible to obtain much valuable insight into the crime, they do not allow Sherlock Holmes and his modern descendants to arrest the perpetrator. Here is exactly where *matrix isolation* steps in. This technique serves to incarcerate Dr. Moriarty and his cohorts who pulled the trigger and to investigate leisurely and in detail his demeanor, his weapons, his motives, and to see if these could eventually be used productively.

However, not all reactive intermediates are kind enough to provide spectroscopic signatures that allow their immediate and unambiguous identification, and it is therefore often necessary to compare those signatures to ones obtained by means of *modeling calculations* (the reader may note that with this we leave the realm of forensic analogy that we have perhaps already stretched too far). In fact, many recent matrix isolation studies owe their success to the tremendous advances in the field of computational chemistry, and to the increased availability of the hard- and software required to carry out such calculations. This situation provides an opportunity for much creative work in the field of reactive intermediates, but it also implies an obligation on the part of those who use such methods to apply them with due care and circumspection.

A productive exploitation of the synergy between experiment and theory requires that practitioners familiarize themselves with the scope and limitations of the methods they use, so they can avoid pitfalls due to *artifacts* that may occur both in experiment and in theory. It is, for example, disturbingly easy to “create” or “annihilate” bands by formation of suitably scaled difference spectra. On the other hand, the harmonic approximation that is at the basis of all practicable modeling calculations of vibrational spectra may lead to predictions that have no relation to experiment (as demonstrated above for the case of phenylcarbene).

Another malicious enemy of good science, which is looming over every spectrometer and computer, is *wishful thinking*. Burdened by expectations one has about the outcome of an experiment, it is often very tempting to pick, say, the peaks in a matrix isolation IR spectrum that appear to correlate with those calculated for an anticipated product (perhaps after a bit of squinting), and to use those peaks as a basis for a structural identification, sweeping others under the proverbial rug as spectroscopic garbage. Not only can this lead to false assignments, but one may miss very important hints that Nature provides on the chemistry that is taking place, and which is often outside the scope of what one originally set out to consider.

It is to be hoped (and, indeed, to be anticipated) that modeling calculations will become more reliable in the future, especially in the area of electronically excited states. However, this will not free us from using these powerful tools critically and circumspectly. With this caveat, a bright future lies ahead of matrix isolation spectroscopy, and there can be no doubt that it will continue to provide much valuable insight, as it has in the past.

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11. Note that fused silica, which has an even higher UV transparency, is not a good choice because of its extremely poor heat conductivity that makes for very inefficient condensation of the host gas.

12. Here the mechanical properties are not so important because the external windows are not subjected to big temperature variations, and they do not need to be clamped down hard because the vacuum inside the cryostat holds them in place.
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