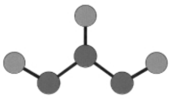
The spectroscopy of molecular reaction intermediates trapped in the solid rare gases


cis-(NO)$_3^-$

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The trapping of neutral and electrically charged molecular reaction intermediates in the solid rare gases and the characterization of these intermediates by vibrational and electronic spectroscopy are surveyed. Spectral data for reaction intermediates trapped in solid neon and argon are compared with the corresponding data obtained from gas phase studies and from quantum chemical calculations. Emphasis is placed on recent progress, including the production, stabilization, and spectroscopic study of highly reactive small molecular ions and the use of *ab initio* and density functional calculations for the identification of reaction intermediates.

1 The reaction intermediate

In most chemical processes, the initially produced atoms or molecules undergo further reactions. If the process consists of sequential reactions, removal of a given reaction intermediate prevents the later stages of the process from occurring; if a branching reaction is present, removal of a reaction intermediate may alter the end product distribution. Because these intermediates react very rapidly, their concentrations are too low for detection using conventional techniques. Consequently, the reaction mechanism has often been inferred by end product analysis, and ambiguities are common. Many reaction intermediates are free radicals, with partially filled molecular orbitals. Typical small free radicals react with a probability between 10^{-3} and 10^{-6} on a single collision. Other reaction intermediates are molecular ions, bearing a positive or a negative electric charge, which often have a much greater probability—between a few tenths and 10^{-2} or less—of reacting on each collision with a reaction partner. Even when there is an initial rapid burst in the concentration of such a species, often the intermediate reacts too quickly to permit its detection by any but the most sensitive techniques.

Marilyn E. Jacox received her PhD degree in physical chemistry from Cornell University and pursued postdoctoral research at the University of North Carolina, Chapel Hill, N. C. In 1958 she moved to Mellon Institute (now a part of Carnegie-Mellon University) in Pittsburgh, Pennsylvania, where she began her spectroscopic studies of chemical reaction intermediates in collaboration with Dr Dolphus E. Milligan. In 1962, she was appointed a Research Chemist at the National Bureau of Standards (now the National Institute of Standards and Technology). Dr Milligan moved there in 1963, and they continued their research collaboration until his death in 1973. During that time, they discovered that molecular ions, as well as free radicals, could be stabilized in rare-gas matrices and used charge transfer of small molecules with alkali metal atoms and photoionization techniques to study the spectra of several different ionic species. Dr Jacox's ongoing research studies in this field have led to the publication of more than 165 papers and one book. In 1996, she was appointed Scientist Emeritus at the National Institute of Standards and Technology. She has received several awards for these studies, among them the 1989 Ellis R. Lippincott Award in Vibrational Spectroscopy. In 1993, she received an honorary ScD degree from Syracuse University.

Infrared and visible–ultraviolet (electronic) spectroscopy are important tools for detecting and studying reaction intermediates. Not only do they permit positive identifications, but for moderate-size molecules the detailed analysis of the gas-phase spectrum permits a quantitative determination of the structure. Electronic spectroscopy provides information for molecules which have one or more electrons promoted to a higher orbital. These electronically excited molecules play important roles in some chemical reactions. When the molecule fluoresces in a region for which laser excitation is possible, laser-excited fluorescence provides an exceptionally sensitive, space and time specific tool for monitoring and studying selected regions of the reaction system. Such studies may also give information on the positions of some of the lower-state or ground-state vibrational energy levels. Infrared spectroscopy gives information on the vibrational energy levels of the molecule in its lowest electronic state. Analysis of this ground-state vibrational energy level pattern gives detailed information about the structure and strengths of the chemical bonds in the molecule.

The possibility of storing spectroscopically detectable concentrations of reaction intermediates in a nitrogen or rare gas solid, or matrix, was first recognized by Whittle, Dows, and Pimentel.[1] These matrix materials are often chemically inert and are optically transparent from the far infrared well into the vacuum ultraviolet. The early experiments demonstrated that at 20 K, a temperature conveniently obtained using liquid hydrogen, solid nitrogen and argon are sufficiently rigid that molecular diffusion and, for dilute solid solutions, subsequent chemical reaction are effectively inhibited. At the cryogenic temperatures required for studying the rare gas solids, molecules reside in their ground electronic and vibrational states. Because diffusion is inhibited, reaction intermediates do not undergo further reaction, and sufficient concentrations of many of them have been obtained for studies of their electronic and infrared spectra.

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Trapping of a molecule in an inert solid may perturb its electronic and vibrational spectrum. In order to determine how useful spectroscopic data obtained for a matrix-isolated reaction intermediate can be for estimating the corresponding data for the gas-phase intermediate, several comparative studies have been reported.

At wavelengths longer than 200 nm, electronic transition origins and vibrational band spacings of molecules trapped in argon and neon matrices typically correspond closely to the gas-phase values. In a comparison of some 230 electronic transitions of diatomic molecules for which both gas-phase and matrix isolation data were available, Jacox[2] found that both the transition origins and the vibrational spacings are shifted by less than about 1% in neon matrices. Somewhat larger shifts, often to longer wavelengths, are typical for molecules isolated in a heavier rare gas or a nitrogen matrix. For relatively large molecules, Bondybey and Miller[3] found that the radiative lifetime on isolation in a rare gas matrix is frequently related to that in the gas phase by a simple refractive index correction. For a neon matrix, this translates into a decrease by approximately 15%. However, small molecules have many fewer energy levels. A significant perturbation of one of these by the matrix may cause a large change in the molecular behavior. For example, in early studies of matrix-isolated C_3, Weltner and McLeod[4] assigned an emission spectrum with origin at 17080 cm^{-1} to the $\tilde{a}\ {}^3\Pi_u$–$\tilde{X}\ {}^1\Sigma_g^+$ transition of C_3. Because the radiative lifetime of C_3 excited to its higher lying $\tilde{A}\,{}^1\Pi_u$ state is reduced at least twentyfold by efficient intersystem crossing when C_3 is trapped in a neon matrix, it is much easier to see the triplet–singlet emission in the neon-matrix experiments than in gas phase studies. The position of the gas-phase band origin, $T_0 = 17090 \pm 210\ cm^{-1}$, was determined many years later.[5] There have been more recent comparisons of gas-phase and neon-matrix electronic spectral data for HCC and for a few larger molecules. The band positions and assignments (obtained from the magnitudes of carbon-13 isotopic shifts) reported by Forney and co-workers[6] for the highly perturbed near-infrared $\tilde{A}\,{}^2\Pi$–$\tilde{X}\,{}^2\Sigma^+$ transition of HCC trapped in a neon matrix correspond closely with those found by Hsu and co-workers[7] for the gas-phase molecule. Maier[8] found that almost all of the Π–Π transitions of neutral and charged species of formula C_n, HC_n, HC_nH, HC_nN, and NC_nN trapped in a neon matrix are shifted to longer wavelengths than the corresponding gas-phase transitions by less than 150 cm^{-1}.

Like the electronic spectrum, the infrared spectrum can provide the basis for development of reaction system probes. Not all molecules have conveniently placed electronic transitions for this purpose. Moreover, poor Franck-Condon overlap with the ground state or the occurrence of such processes as predissociation may prevent the use of an electronic transition for highly sensitive laser-excited fluorescence measurements. In contrast, all molecules except homonuclear diatomics possess infrared absorptions.

Vibrational transitions usually occur in spectral regions characteristic of specific types of bonding. Where there are exceptions to this generalization, as sometimes happens for species with incompletely occupied molecular orbitals, analysis of the spectrum can give valuable information on the nature of the chemical bonds.

Infrared absorptions of molecules trapped in neon or argon matrices are sharp, with typical line widths (FWHM) on the order of 1 cm^{-1}. Although molecules may be trapped in several different types of sites in the solid rare gas, usually one or two major sites predominate, with an associated spectral splitting of only a few cm^{-1}.

Jacox[9] has compared the positions of ground-state vibrational fundamentals of diatomic molecules in the gas phase with those in rare gas and nitrogen matrices. Except for van der Waals molecules and for the Group Ia and IIIa halides, the argon-matrix shifts of most diatomic molecules are less than 2%. Smaller matrix shifts are observed for solid neon. Since a substantial amount of new data is now available for diatomic oxides, a revised comparison is offered in Fig. 1. There remain many gaps in the data shown in this figure. Most often, the gas-phase data are missing. A series of experiments conducted by Andrews and co-workers on the reaction of laser-ablated transition metal atoms with oxygen has yielded argon-matrix and sometimes neon-matrix values for the positions of the ground-state fundamentals of many of the diatomic oxides. Similar studies have also been conducted by this group for the diatomic hydrides and nitrides. Except for ZrO, all of the neon-matrix shifts are less than 1%. Relatively large argon-matrix shifts occur for the Group IIa oxides, as well as for AgO and YbO. (References to individual oxides are available from the NIST Chemistry WebBook.)

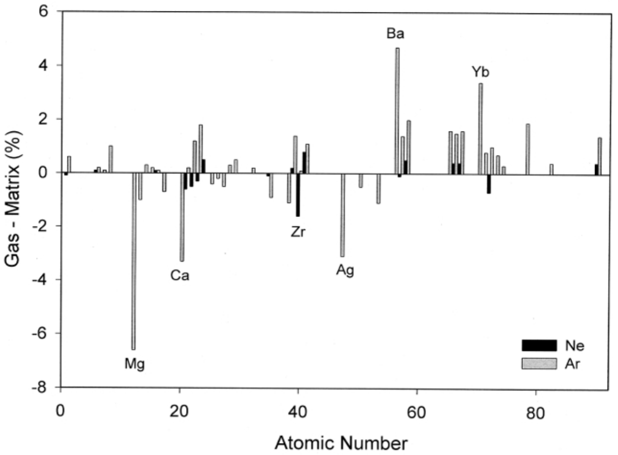

Fig. 1 Neon- and argon-matrix shifts for ground-state vibrational fundamentals of diatomic oxides.

Jacox[10] has also compared the positions of the ground-state vibrational fundamentals of diatomic and polyatomic reaction intermediates observed in the gas phase with those observed in neon and argon matrices, including consideration of the relationship between magnitude of the matrix shift and type of vibration. An updated comparison is shown in Fig. 2. As was previously reported, most spectral shifts in these two matrices are less than about 1%. For a neon matrix, the average numerical

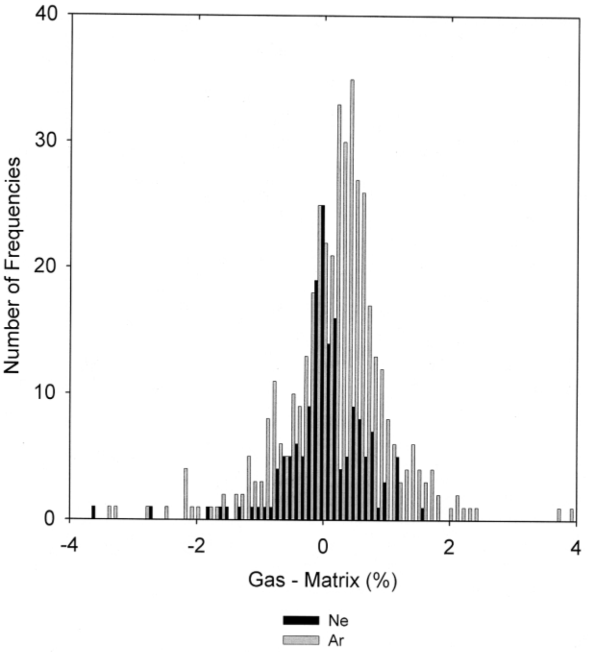

Fig. 2 Neon- and argon-matrix shifts in ground-state vibrational fundamentals of transient molecules.

deviation is −0.03%, the average absolute deviation is 0.42%, and the standard deviation is 0.41%. For an argon matrix, the average numerical deviation is 0.21%, the average absolute deviation is 0.65%, and the standard deviation is 0.87%.

With the growth in capacity of computational facilities and sophistication of computational procedures, quantum chemical calculations show promise of becoming reliable predictors of vibrational and electronic energy levels of reaction intermediates. Byrd and co-workers[11] have compared the experimentally determined ground-state structures and vibrational fundamental frequencies for 33 diatomic and small polyatomic free radicals with the values predicted by several frequently used *ab initio* and density functional calculations, performed using 6-31G(d,p), cc-pVDZ, and cc-pVTZ basis sets. Of particular interest here are the frequency comparisons, for which 93 experimental-computational pairs were available. The influence of the level of the calculation was most important; basis set effects were relatively modest. Hartree-Fock and MP2 calculations gave erratic results. In the following discussion, only the results of unrestricted calculations will be considered. The average deviations for calculations performed at the CCSD, CCSD(T), and B3LYP levels using selected basis sets are shown in Fig. 3, together with neon- and argon-matrix deviations from the gas-phase band centers for the same set of frequencies. The average numerical deviations given for the computational results have the reverse sign from those given in Fig. 2. For consistency with the values of Byrd and co-workers, in determining the average numerical deviations of the experimental data given in Fig. 3 the factor (Ne − gas) or (Ar − gas) rather than its negative was used. For the neon matrix, 17 comparisons were available, and for the argon matrix, 29. While these numbers are relatively small, the resulting average numerical deviations are consistent with those given in the discussion of Fig. 2. The B3LYP calculations yield results comparable to those of the considerably more computationally expensive CCSD calculations. In terms of the average numerical deviations, the most satisfactory procedure is also the most sophisticated one, CCSD(T)/cc-pVTZ. However, the spread of the deviations for this procedure, measured by the average absolute deviations and by the standard deviation, is comparable to that for several of the other procedures. The neon- and argon-matrix observations deviate from the gas-phase band centers by less than one-fifth as much as do any of the calculations included in the comparison, and the spread in their deviations is less than 1%.

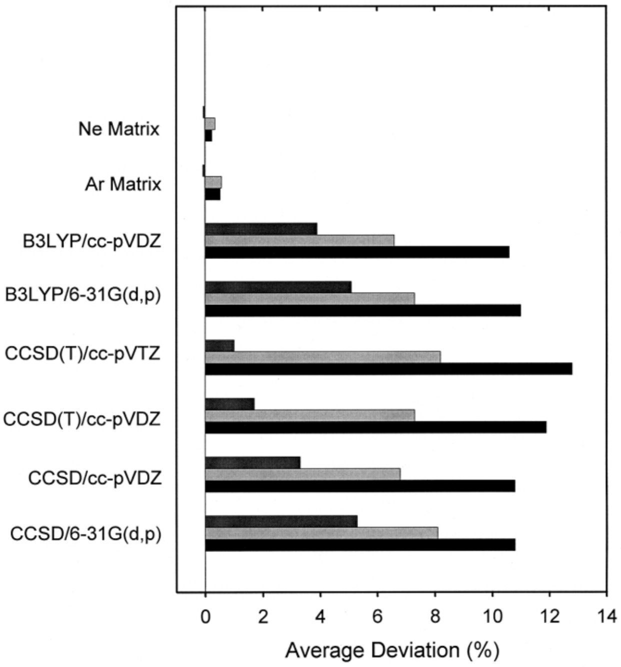

Fig. 3 Average deviations of neon- and argon-matrix frequencies and of unrestricted calculations of vibrational fundamentals of free radicals from observed gas-phase values. (Frequency set and values for quantum chemical calculations from Ref. 11. In each group, top = num. av., middle = abs. av., and bottom = std. dev.)

A major contributor to the deviations for the computational procedures is comparison of the computed harmonic vibrational frequencies with experimentally determined anharmonic ones. Data are usually insufficient for ascertaining the harmonic vibrational frequencies of molecules larger than diatomic. Byrd and co-workers[11] also compared the average deviations for the subset of 13 diatomic free radicals for which harmonic vibrational fundamentals had been derived from the experimental data. The average numerical deviations for the unrestricted CCSD, CCSD(T), and B3LYP calculations using the cc-pVTZ basis set were significantly improved, to 3.9%, 0.9%, and 3.1%, respectively. Most of the average absolute deviations and standard deviations for these three procedures were between 3% and 4%.

In summary, calculations at the B3LYP, CCSD, and CCSD(T) levels can serve as valuable predictors of the positions of the ground-state vibrational fundamentals of gas-phase free radicals. However, where neon- or argon-matrix values are available, they can significantly refine these estimates. The matrix data can also be useful for developing further refinements of computational procedures.

The following discussion will be limited to infrared, visible, and ultraviolet studies of small polyatomic reaction intermediates trapped in solid argon and neon. Emphasis will be placed on principles and on results obtained since 1990. An earlier review[12] has offered a detailed consideration of the role of the matrix cage and of the use of matrix isolation for studying the products of atom–molecule reactions. Matrix isolation experiments are extremely valuable for the identification and characterization of larger organic reaction intermediates. Many previously undetected prototypes of uniquely bonded types of molecule, including *m*-benzyne and *p*-benzyne,[13] have been stabilized and studied in rare-gas matrices. Evaluated infrared and electronic spectral data for over 2000 such species are included in published compilations by Jacox.[14,15] The field is advancing rapidly. Even more up-to-date information is available on the Internet as a part of the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/).

2 Stabilization of reaction intermediates

2.1 Role of the cage effect

A large body of experiments has demonstrated that atoms can undergo at least limited diffusion in the solid rare gases, but that at sufficiently low temperatures molecules are trapped.[12] Atoms can also recombine at the site of their production, sometimes resulting in the formation of an isomeric product. For example, when H + CN are produced by vacuum ultraviolet photolysis of HCN in a rare gas or nitrogen matrix, some of these fragments undergo cage recombination to form HNC. Atoms formed with sufficient kinetic energy may escape from the site of their production, leaving a trapped molecular fragment. The diffusing atom may in turn react with another species present in the system, as in the reaction of H atoms with O_2 to form HO_2. When photodissociation of a precursor molecule results in the formation of a pair of molecules trapped in adjacent sites, their stabilization occurs only if the activation energy for the reverse recombination is small. This phenomenon sometimes leads to isomerization, as in the appearance of HOCN upon 254 nm irradiation of matrix isolated HNCO. When a high-energy molecule which may rearrange or predissociate is formed in the gas phase and rapidly frozen in a solid rare gas or when it is formed in the surface layers of the deposit, that species may experience collisional deactivation by the argon or neon atoms before such a change can occur, altering the product distribution from that characteristic of the gas phase.

2.2 Production and properties of molecular ions

Before 1990, knowledge of the spectroscopic properties of molecular ions was largely confined to a few types of species. Gas-phase discharge systems had yielded a considerable body of information for diatomic cations, as well as information for a few polyatomic cations, including CO_2^+, OCS^+, CS_2^+, $C_4H_2^+$, and several haloacetylene cations. Sophisticated infrared laser experiments—primarily in the laboratories of Oka, Saykally, and Amano—had permitted study of the H-stretching fundamentals of H_3^+ and a few other small protonated molecules. Matrix isolation studies in several laboratories had produced infrared data for HAr_2^+, HKr_2^+, and the halomethyl and halomethane cations, and laser-excited fluorescence results were available for a number of halobenzene cations. The only gas-phase anion that had been reported was C_2^-. That species and a few small polyatomic anions, including NO_2^-, O_3^-, $ClHCl^-$, and $BrHBr^-$, had been studied in rare-gas matrices. As will be seen, recent developments have permitted infrared studies of a considerable number of small molecular ions with more diverse composition and chemical bonding properties. These studies have included systematic surveys of the infrared spectra of anions and cations formed from molecules in the earth′s atmosphere (including the nitrogen oxides), ions which can be formed in plasma processing (including those derived from the inorganic fluorides), ions formed from small hydrocarbons such as acetylene and allene, and ions formed from the first members of homologous series, such as the methyl halides.

Measurements of the infrared spectra of small molecular ions promise to extend our knowledge of the properties of these species. It is often presumed that the vibrational energy levels of ground-state molecular ions are similar to those of the parent neutral molecule. However, this presumption is not always valid. Although they are widely available, photoelectron spectra provide only limited vibrational data. Unless the geometries of the neutral and ionic species differ considerably there may be little vibrational structure in a photoelectron band. Structure in the photoelectron spectrum is often poorly resolved, and, except for threshold photoelectron studies, uncertainties are likely to range between 10 and 100 cm^{-1}. Because the selection rules are different, infrared spectral data are generally complementary to data obtained from fluorescence or photoelectron spectral observations.

The first technique used for ion stabilization in rare-gas matrices was collisional or photoinduced charge transfer between alkali metal atoms and a suitable electron acceptor. These experiments permitted the stabilization of a number of important molecular anions, including C_2^-, NO_2^-, and $ClHCl^-$. However, it was soon found that the relatively mobile metal cation may form a complex with the adjacent anion. For example, $Ar{:}SO_2$ samples codeposited with sodium atoms show prominent absorptions of $Na^+SO_2^-$, for which the antisymmetric SO_2^- stretching absorption lies approximately 50 cm^{-1} below that of the uncomplexed anion. The radially symmetric atomic cation field may also split degenerate fundamentals of species such as NO_3^-, leading to erroneous structural inferences.

While exposure of the sample to sufficiently energetic vacuum ultraviolet radiation can result in photoionization, only rarely is an appreciable ion yield obtained when a previously deposited sample is irradiated. Absorption coefficients in the vacuum ultraviolet region are typically very high, and products formed in the surface layers of the deposit shield the inner layers from photoionizing radiation. To circumvent this problem, concurrent deposition and irradiation are often conducted.

Although discharges are an effective means for ion production, experiments in which the whole sample is put through the discharge and subsequently frozen at cryogenic temperatures are fraught with difficulties. Extensive atomization and isotopic scrambling occur. A few strongly bound diatomic and small polyatomic species, such as C_2, N_2, CO, CN, and C_3, may survive and/or be formed, and in the quenching process may further react. Moreover, the possibility of energy overload and consequent poor isolation must be considered. Discharge products such as H_2 may not be trapped efficiently on the cryogenic sampling surface. When argon, krypton, or xenon is used as the matrix material, charge exchange is likely to occur; cations formed from species with ionization potentials greater than those of these rare gases may lose their electric charge to the rare gas. Incipient reactivity of the molecular cation with the heaver rare gases also may lead to large matrix shifts. As will be seen, this is sometimes true even for neon.

Many of these difficulties can be avoided if the discharge is excited in a pure rare gas, the ion precursor is introduced farther along the flow stream, and the interaction products are rapidly frozen onto the cryogenic observation surface. Such a configuration was used by Jacox and Thompson,[16] who found that when neon was passed through the discharge sufficient concentrations of CO_2^+ and CO_2^- were stabilized in the neon matrix for study of their infrared spectra. In these experiments, the precursor molecule may interact either with the rare gas resonance radiation or with rare gas metastables, which have relatively long lifetimes. Photoionization or Penning ionization, respectively, results. The energies of the first excited states of the neon atom, between 16.6 eV and 16.85 eV, are sufficiently great to permit ionization of any uncharged species except helium and neon itself. Photoionization products trapped in solid neon have been observed with this sampling configuration for a number of molecules with exceptionally high ionization potentials, including BF_3 and HF. Observations on many systems indicate that the parent molecule remains outside the discharge region. Fragment ions with appearance potentials above 16.85 eV are not observed. Extensive photofragmentation and isotopic randomization do not occur. Electrons produced on photoionization are captured by other species in the system, so that the overall deposit is electrically neutral. Infrared absorptions of the resulting anion species may also appear in the sample.

Matrix properties which are desirable to minimize ion–matrix interactions include a high ionization potential, a low polarizability, a near-zero electron affinity, and a low proton affinity. All of these properties are optimal for the neon matrix. The distribution of neon matrix shifts heretofore determined for the ground-state vibrational energy levels of cations is shown in Fig. 4. As was found for uncharged reaction intermediates, most cation matrix shifts amount to less than about 1%. Insufficient gas-phase data are available for the corresponding anion comparison.

Laser ablation, long recognized as suitable for the preparation of uncharged atoms and molecules from refractory materials, has recently been found to be useful for the stabilization of molecular ions in a matrix environment. Bondybey and English[17] first used the laser vaporization of lead for gas-phase studies of the laser-excited fluorescence spectrum of Pb_2. Shortly thereafter, Bondybey[18] applied laser vaporization to studies of the spectrum of laser-excited SiC_2 both in the gas phase and isolated in a neon matrix. Laser ablation has recently been used by Andrews as a metal atom source for systematic studies of the infrared spectra of the products of reaction of transition and rare-earth metal atoms with H_2, N_2, O_2, CO, and NO trapped in argon, neon, and nitrogen matrices. Other studies by the Andrews group have been concerned with the infrared spectra of the reaction products of Group II and III metals with

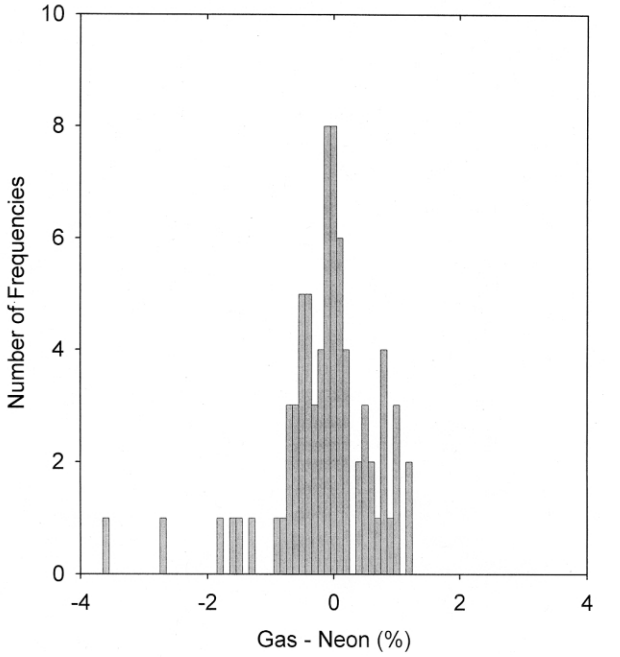

Fig. 4 Neon-matrix shifts in ground-state vibrational fundamentals of molecular cations.

various small molecules trapped in these matrices. Even in the early studies, it was recognized that excited-atom reactions occurred, so that the extent of reaction of laser-ablated atoms is often greater than that for the same atomic species vaporized from a Knudsen cell. In the more recent studies, it has been found that the metal atoms or other refractory species may be formed with sufficient energy to lead to ion production. Electrons thus released can be captured by molecules present in the system. Results for many neutral and charged transition-metal carbonyl species have recently been reviewed by Zhou and co-workers.[19] The neon matrix provides the most favorable environment for ion stabilization in laser ablation experiments. However, a number of anions have been identified in argon-matrix experiments. The infrared absorptions for several anions, including *cis*- and *trans*-ONNO$^-$ and OONO$^-$, have been found by the Andrews group to be independent of the transition metal used for the experiment, indicating that the transition metal is not present in those anion products.

The chemical bonding of ground-state molecular ions may be different from those of the uncharged species with the same empirical formula. Although HCN is more stable than HNC, the reverse is true for the corresponding cations. In some such systems, the barrier to rearrangement is sufficiently high and the probability of deactivation by the matrix sufficiently great that the parent ion rather than the more stable ion isomer is observed. Thus, HCN$^+$ rather than HNC$^+$ is initially stabilized when HCN is photoionized and the products are rapidly quenched in solid neon. In similar studies of the methyl halides, for which H_2CXH^+ (X = F, Cl, Br) is the more stable cation isomer, infrared absorptions of all three H_2CXH^+ species have been detected. Although no infrared absorptions of CH_3F^+ were identified, sufficient CH_3Br^+ was stabilized for the detection of all nine of its vibrational fundamentals. (The three doubly degenerate fundamentals are split because of Jahn-Teller interaction.)

Because ion-molecule reaction rates are typically very large, it is often possible to study the infrared spectra of dimer cations and anions, as well as of ion–molecule complexes such as $O_2C\cdots O_2^-$. Indeed, weak infrared absorptions of a trimer anion, $(NO)_3^-$, have also been identified.

The study of photodestruction processes which result from secondary irradiation of the deposit is exceptionally valuable. Photodissociation and photoisomerization of both neutrals and ions may occur. Cage recombination of molecular fragments may suppress net photodestruction. Thus, although in the gas phase visible radiation photodissociates O_4^+ into $O_2 + O_2^+$, in neon-matrix studies cage recombination is efficient. Photodetachment of anions often, but not always, occurs at an energy below 3 eV. The observed photodetachment threshold for anions trapped in solid neon is usually 1 or 2 eV higher than the gas-phase photodetachment threshold, because low-energy electrons may more readily recombine than escape from the site of their release. Some of the electrons detached from anions may diffuse through the matrix and neutralize cations, reducing their concentration.

2.3 Distinguishing anions from cations

Several strategies are available for distinguishing anions from cations in matrix isolation experiments. Where the spectrum of the gas-phase ion is known, a good correspondence of the matrix absorption pattern provides strong supporting evidence for the ion identification. For some molecules, ionization or electron attachment results in a large change in chemical bond strength, shifting one or several infrared absorptions into a different, characteristic spectral region. Photodestruction behavior is sometimes useful; the absorptions of the uncharged species may grow in intensity as the ion absorptions are destroyed, or infrared absorptions of a characteristic photofragment may appear. Thus, visible irradiation of a neon-matrix deposit containing BF_3^+ leads to the appearance of a prominent absorption of BF_2^+. The addition of a supplementary electron donor (*e.g.*, Na, K, Cs) may result in enhanced concentrations of anion species. Addition of a supplementary electron captor such as NO_2 or a chloromethane may enhance the concentration of cations which are stabilized and/or extend the wavelength range of stability of cations on exposure of the sample to visible/ultraviolet radiation. With a chloromethane dopant, Cl atoms are the effective electron captors. When NO_2 is used as the electron trap, detectable growth in the infrared absorption of NO_2^- may occur as photodetachment of the less strongly bound anion proceeds. Where several different anion species are important, it is sometimes possible to selectively photodetach one of them. After that anion has been destroyed, on prolonged irradiation in the same wavelength range the cation concentration will level off at the new, lower value. The process may sometimes be repeated at somewhat larger photon energies, with more extensive but still incomplete photodestruction of the cations. At sufficiently high photon energies, photodestruction of both anions and cations is complete.

Mass selection is helpful for simplifying the composition of the matrix deposit, but has heretofore proved less useful for isolating individual charged species. One of the earliest mass selection studies, by Forney, Jakobi, and Maier,[20] succeeded in stabilizing sufficient concentrations of C_2^+, NCCN$^+$, and ClCCCl$^+$ in a neon matrix for detection of their electronic spectra. In another early study,[21] the electronic spectrum of matrix-isolated Ag_2 was obtained by mass selection of Ag_2^+ and subsequent neutralization by electrons. Lindsay and Lombardi later studied the visible/ultraviolet and resonance Raman spectra of many other small metal clusters formed in this way. Subsequently, Halasinski and co-workers[22] detected the infrared absorption of the ν_3 fundamental of matrix-isolated CF_3^+ in a mass selection study. In such studies it is always necessary to consider possible complications beyond the mass selection stage, such as fragmentation and reaction of the ion with water and other impurities desorbed from the walls of the system during the very long time usually needed for the sample deposition. When only cations or anions are deposited in the matrix, after a very short time a high repulsive potential to further ion deposition develops. Other processes may occur which lead to at least approximate charge neutrality of the overall deposit. The Maier group detected flow of electric current in the system. Halasinski and co-workers later obtained evidence for electron capture by impurities such as CO_2, which, like H_2O, may desorb from the walls of the vacuum system. They enhanced their cation signals, as well as the infrared absorption of CO_2^-, by adding a small amount of CO_2 to the matrix gas.

3 Identification of reaction intermediates

Isotopic substitution is the 'gold standard' for achieving positive identifications of reaction intermediates in a matrix environment. Vibrational fundamentals of species with partially filled electron orbitals sometimes lie at frequencies quite different from those characteristic of stable molecules. Isotopic substitution experiments verified that the CH-stretching fundamental of HCO, an important combustion reaction intermediate, lies below 2500 cm^{-1} and that the antisymmetric stretching fundamental of N=C=N lies near 1475 cm^{-1}.

Photolysis of the initial deposit with filtered radiation is also useful in product identification. Such studies permit sorting of the peaks by photolysis threshold and determine the photolysis products.

Kinetic arguments are insufficient for positive identification of matrix-isolated molecules. A classic example of their failure is in the early 'HNO' identification. Gas-phase studies showed that HNO was formed by the flash photolysis of nitromethane. Accordingly, Brown and Pimentel[23] proposed a complete vibrational assignment for HNO, formed by the photodecomposition of nitromethane (CH_3NO_2) or methyl nitrite (CH_3ONO) in an argon matrix at 20 K. Later studies by Müller and co-workers[24] demonstrated that two of the three 'HNO' fundamentals were instead contributed by nitrosomethanol, $CH_2(NO)OH$, and showed carbon-13 shifts. This group assigned the *cis*- and *trans*- stereoisomers of nitrosomethanol, and were able to study a reversible photoconversion between the two forms.

Ab initio calculations have proved very useful in the identification of reaction intermediates formed in matrix isolation experiments. However, the differences between calculated and observed vibrational frequencies may be sufficiently great to weaken arguments for the positive identification of closely related species based on the relative positions of their calculated fundamental vibrations. Moreover, good agreement between the observed and calculated absorption pattern is not a sufficient condition for the positive identification of the carrier of the spectrum. Problems are especially likely to arise in distinguishing between various isomers and between products with similar elemental compositions but different numbers of atoms of one or more of these elements. An example is provided by the $(NO)_3^-$ anion,[25] which possesses the two almost isoenergetic structures designated in Fig. 5 as the *trans*- and *cis*-stereoisomers. The three infrared absorptions of the product of this composition which were observed in the neon matrix were somewhat closer to the values obtained in B3LYP/6-311 + G(d) calculations for the *trans*-isomer than to those obtained for the *cis*-isomer. However, as is shown in Fig. 6, the patterns of absorptions observed for these three vibrational fundamentals in isotopically enriched mixtures were in excellent agreement with the patterns calculated for the *cis*-isomer but in poor agreement with those for the *trans*-isomer. An excellent example of the synergy of experiment and density functional calculations for isotopically substituted species is provided by the recent study by Maier and co-workers,[26] in which this strategy resulted in the infrared identification of seven different products of the reaction of silicon atoms with N_2, a system for which only one product had previously been identified. Nevertheless, one *caveat* remains; where two moieties are weakly coupled, even detailed isotopic substitution studies may fail to determine which of two different structures is preferable. The mid-infrared isotopic substitution patterns of weakly bound dimer species cannot distinguish between such isomers as *cis*-O_4^- and *trans*-O_4^-. An experimental distinction would require study of the low-frequency vibrational fundamentals which involve the bonds coupling the weakly bound moieties.

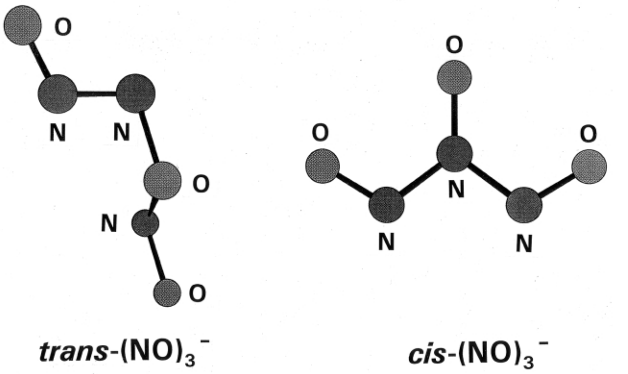

Fig. 5 Structures of *trans*-$(NO)_3^-$ and *cis*-$(NO)_3^-$.

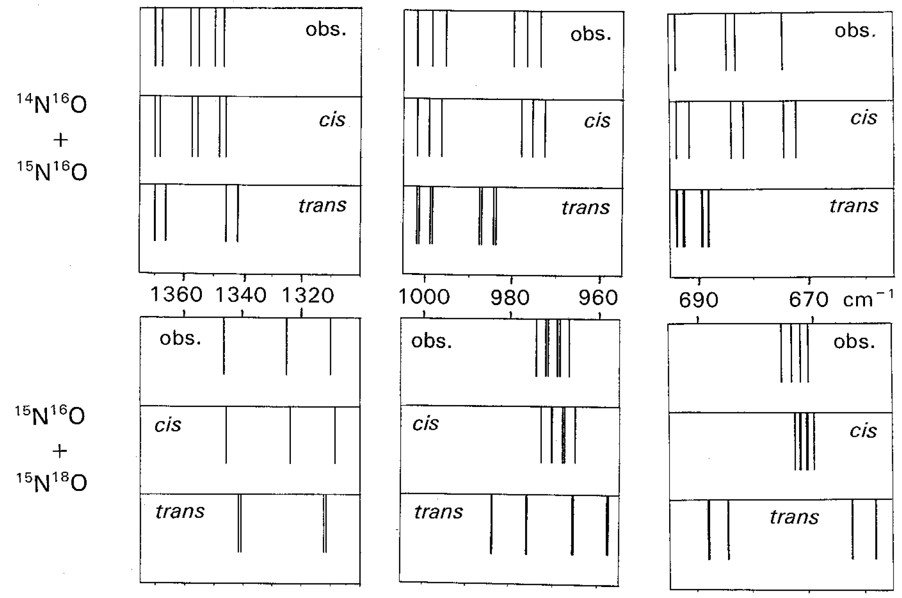

Fig. 6 Positions (cm^{-1}) of observed $(NO)_3^-$ absorptions in mixed-isotopic experiments compared with B3LYP/6-311 + G(d) values for *cis*- and *trans*-isomers. The calculated values for each fundamental were scaled so that the calculated and experimental values for that fundamental of $(^{14}N^{16}O)_3^-$ are equal.

4 Properties of special interest

4.1 Production of uncharged molecules containing rare gas atoms

Even rare gas matrices are not always inert. Although the rare gases are most likely to react with ionic species, two recent discoveries highlight their potentially strong interactions with uncharged molecules. Xenon matrices may facilitate spin conversion, a phenomenon which has been considered in detail by Maier and Lautz.[27] Experiments in the laboratory of Räsänen have demonstrated the stabilization of a number of uncharged species of formula HRgX in rare-gas matrices. In these experiments, a hydride, HX or HXY, is photodissociated in a rare-gas matrix, usually krypton or xenon, using an excimer laser or a vacuum ultraviolet discharge lamp. On controlled warmup of this deposit, followed by recooling, prominent infrared and ultraviolet absorptions of HRgX or HRgXY appear.[28] Recently, the first uncharged argon compound, HArF, was made in this way.[29,30] Its initial infrared spectral identification was supported by extensive isotopic substitution, including the use of isotopes of argon. The identification is consistent with the results of *ab initio* calculations.

4.2 Phenomena unique to molecular ions

The extraordinarily high reactivity of molecular ions often leads to the stabilization of spectroscopically detectable concentrations of the products of ion–molecule reactions in the matrix. These cluster ions are commonly intermediate in bond strength between van der Waals molecules and typical single bonds. A number of such complexes, including O_4^+, O_4^-, and $O_2C{\cdots}O_2^-$, have been mentioned in this review. Gas-phase spectroscopic data for such species are sparse. It is anticipated that vibrations involving weak bonds may be relatively strongly perturbed by the matrix. However, the antisymmetric NN-stretching vibration of N_4^+, which is relatively strongly bound, exhibits only a very small matrix shift. Further measurements of the infrared absorption patterns of ion–molecule complexes should greatly extend our knowledge of the structures of these species and should provide spectroscopic information necessary for developing optical diagnostics.

The raising of the effective threshold for electron photodetachment from anions trapped in neon matrices may facilitate the detection of anion transitions above the photodetachment threshold. Recently, Lakin and co-workers[31] have studied Feshbach resonances of neon-matrix isolated C_3^- and C_5^-.

An important class of ion–matrix interactions is that of proton sharing between the rare gas atom and a protonated species, MH^+. Bieske and Dopfer[32] have recently reviewed this phenomenon, which often results in large shifts in H-stretching vibrations of gas-phase clusters of MH^+ with one or more rare gas atoms. The largest shift is generally observed for complexation with a single rare gas atom, with somewhat smaller shifts for larger clusters. Shifts amounting to several hundred cm^{-1} are frequently observed for complexes in which the difference between the proton affinity of M and that of the rare gas atom is relatively small. The extent of such shifts for gas-phase clusters and for matrix isolation systems involving neon and argon is summarized in Fig. 7. Shifts characteristic of interaction with argon atoms are substantially larger than those for interactions with neon atoms. The proton affinity of the argon atom is 369.2 kJ mol^{-1}, while that of the neon atom is 198.8 kJ mol^{-1}. When the abscissa is the difference between the proton affinity of M (from which MH^+ is derived) and that of the rare gas, as in Fig. 7, the plot of the shifts for interactions with argon and neon is approximately exponential. Because the proton affinity of helium, 177.8 kJ mol^{-1}, differs relatively little from that for neon, substantial shifts in the vibrational transitions of some protonated species occur even in helium clusters. Proton affinities of most molecules are greater than 500 kJ mol^{-1}. However, that for the F atom is only 340.1 kJ mol^{-1}. Proton sharing between the F atom and the neon matrix is sufficiently important that infrared absorptions of $NeHF^+$ appear.[33] Spectra of the products of proton reactions with rare gas atoms have been known for some time. In the gas phase, detailed assignments of electronic transitions of RgH^+ species are available. For many years, the HRg_2^+ species, which predominate at higher rare-gas pressures, have been familiar to the mass spectrometrist. Infrared absorptions of HAr_2^+, HKr_2^+, and HXe_2^+ trapped in rare-gas matrices have been studied in several laboratories.

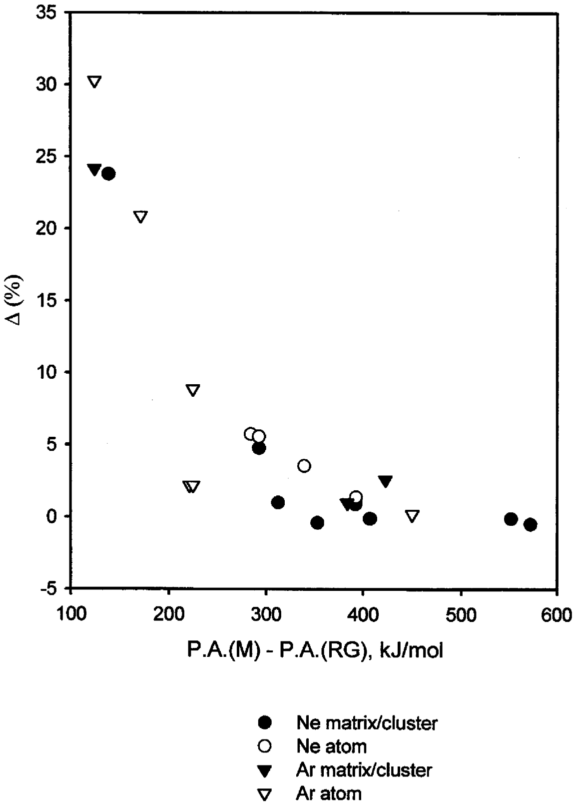

Fig. 7 Shift in the H-stretching fundamental vibration of MH^+ on interaction with a rare-gas atom or matrix.

Ions sometimes experience other types of reaction with rare gases. The mass spectrometry literature contains studies of many diatomic and small polyatomic cations which include a rare gas in their composition but which have yet to be spectroscopically characterized.

5 Outlook

This review provides a very abbreviated survey of the rich world of chemical reaction intermediates. These species are the enablers for chemical processes as diverse as simple inorganic reactions and complicated organic chemical systems. Spectroscopic studies of reaction intermediates in rare gas matrices have yielded information on the structures and chemical bonding properties of many small molecule reaction intermediates, and promise to continue to do so. The correspondence between the positions of their infrared absorptions in the gas phase and in neon and argon matrices is sufficiently close that, where gas-phase data do not exist, matrix data may be useful in further refining quantum chemical computational procedures for species with partially filled orbitals. Spectral identifications of reaction intermediates trapped in rare gas matrices also can aid in the search for these intermediates in gas-phase reaction systems. It is hoped that this work will spur the development of these interesting and important computational and gas-phase studies.

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