CHAPTER 1

PHOTOEXCITATION OF FREE RADICALS AND MOLECULAR IONS TRAPPED IN RARE-GAS SOLIDS

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The photochemical production of free radicals, molecular ions, and other highly reactive species, their trapping in rare-gas solids for studies of their vibrational and electronic spectra, and the use of secondary photolysis for product identification are surveyed. The application of gas-phase thermodynamic and spectroscopic data in planning and interpreting the experiments is emphasized and illustrated.

1. Introduction

Photoexcitation of a suitable precursor is widely used in matrix isolation experiments to prepare free radicals and molecular ions and to study their spectra and photolysis properties. The study of changes in the spectrum of the initial deposit when the sample is later exposed to filtered visible or ultraviolet radiation aids greatly in identifying the products obtained in attempts to generate molecules of interest, chemical reaction intermediates, free radicals, or molecular ions. When the radiation source is sufficiently intense, secondary photolysis products may appear even after the initial irradiation. Often the selection of wavelength ranges for subsequent irradiations has been quite empirical, with the principal objective to simplify the spectral analysis by sorting the product absorptions into categories corresponding to changes in intensity during a given irradiation or sequence of irradiations. However, this selection is most effective when the processes which can occur in the matrix

environment as a result of various sets of irradiation conditions are considered.

This chapter is intended to provide examples of the use of photon sources both for generating free radicals and molecular ions in rare-gas matrices and for planning the strategy for subsequent irradiation of these matrix deposits.

2. Photoexcitation as a Source of Free Radicals

In the early days of matrix isolation studies, photodetachment of N_2 from diazomethane and azides using a medium-pressure mercury arc as the radiation source was believed to be one of the most promising avenues to free radical production. However, the results of these first experiments were disappointing. Among the early workers was Dolphus E. Milligan, who believed that the difficulty in using these species as sources of free radicals arose from cage recombination, which could be a major process when the barrier for the reverse recombination is low. Nevertheless, he found a few azide precursors which yielded stable free radicals. The first of these was ClN_3, which when photolyzed in an argon matrix yielded NCl.[1] Although the expected product of photolyzing CH_3N_3 in solid argon was CH_3N, that product rapidly isomerized to CH_2=NH.[2] A few years later, the importance of cage recombination was confirmed by Moore and Pimentel,[3] who detected the infrared absorptions of $CH_2{}^{15}N_2$ when they photolyzed a deposit of unenriched matrix-isolated diazomethane when $^{15}N_2$ had been added to the sample mixture.

In some systems, isomerization was observed upon cage recombination. Mercury-arc irradiation, for which the most intense emission is near 254 nm, led to the stabilization of HOCN in a deposit of matrix-isolated HNCO.[4] Gas-phase studies had indicated that near 254 nm the primary photodecomposition products of HNCO are NH + CO. In a supplementary study of the photolysis of an Ar:CO:HN_3 deposit, for which the primary photoproducts are NH + N_2, both HNCO and HOCN appeared. This observation suggests that in both systems initially formed NH may react with CO to form an unstable complex.

When an atom is photodetached from a molecule trapped in the solid, it may have sufficient kinetic energy to diffuse from the site of its

photoproduction and to react with another suitable molecule which is also present in the solid. Photodetachment of an H atom from HI, HBr, or H_2S by 254-nm radiation occurs readily. In 1963, Milligan and Jacox succeeded in stabilizing HO_2, an important atmospheric and combustion reaction intermediate, by 254-nm photolysis of an Ar:O_2:HI sample deposit.[5] Detailed isotopic substitution studies — extremely important to positive product identification — confirmed the identification and demonstrated that the two O atoms of HO_2 are inequivalent.

The species which results from atom photodetachment often is itself a free radical. Higher-energy photolysis sources are usually required for atom photodetachment, leaving the desired product. Appropriate radiation sources include the rare-gas resonance lamps and a microwave-excited hydrogen discharge lamp, for which the design was described by Warneck,[6] which provides a high-intensity 122-nm radiation source. This lamp was first applied to matrix isolation experiments to produce NH_2, starting from an Ar:NH_3 sample,[7] and CH_3, starting from an Ar:CH_4 sample.[8] Still another example of H-atom detachment and subsequent diffusion is provided by the 122-nm photolysis of HNCO,[9] in which the predominant product was NCO rather than the HOCN stabilized at lower photon energies. In these and other vacuum-ultraviolet photolysis experiments, it is necessary to photolyze the sample as it is being deposited, in order to reduce screening of the effective radiation from the precursor molecules by the very strongly absorbing Rydberg bands of molecules in the deposit.

Cage recombination sometimes occurs even at relatively high photon energies. In studies on the vacuum ultraviolet photolysis of Ar:XCN samples (X = H, F, Cl, Br), prominent ultraviolet absorption by CN appears, but the XNC isomers of the starting molecules are also stabilized.[10]

Because free radicals have partially filled electron orbitals, many radicals have excited electronic states to which transitions can occur in the visible and near-ultraviolet spectral regions. Excitation into these states may dissociate the radical, isomerize it, or alter its reactivity with a neighboring molecule.

It is sometimes assumed that once a photodecomposition threshold is reached photolysis of the species of interest at higher energies will

proceed to give the same products. However, often sufficient Franck–Condon overlap to support this generalization occurs over only a limited energy range. The first band system of HCO extends from 860 to 460 nm. The bands are diffuse because of predissociation to form H + CO. The origin of a nondiffuse band system lies near 260 nm. Because the bands in this higher-energy system are ubiquitous in hydrocarbon combustion, they have become known as the hydrocarbon flame bands. Matrix isolation experiments using photolysis sources with their major output at wavelengths shorter than 460 nm permit the stabilization of HCO and the detailed study of these hydrocarbon flame bands,[11] assisting in the vibrational assignment of this band system.

A recent example of the occurrence of reaction on photoexcitation is provided by the stabilization of NO_3 in a neon matrix in the laboratories of Jacox[12] and of Beckers and Willner.[13] The well-known $\tilde{B}\ ^2E'$ state of NO_3, which lies 663 nm above the ground state, is strongly predissociated. Both NO and NO_2 are produced. When Ne:NO and Ne:O_2 mixtures are deposited through separate jets to minimize oxidation of the NO to NO_2 and the deposit is exposed to radiation of wavelength shorter than the high energy limit of the NO_3 $\tilde{B}$ state, absorptions of NO_3 appear. The NO_3 yield can be optimized by warming the deposit to approximately 7 K for a few minutes to permit limited reorientation and diffusion of the molecules in the neon matrix. When this NO_3 is exposed to visible radiation in the 450–663-nm wavelength range of its $\tilde{B} - \tilde{X}$ transition, it is destroyed, and absorptions appear within a few cm^{-1} of the positions of the NO absorption and the band center of the infrared-inactive fundamental of O_2. This suggests the stabilization of a very weakly bound $(O_2)(NO)$ complex in the neon matrix. Exposure of the resulting sample to radiation of wavelength shorter than the high energy limit of the NO_3 $\tilde{B}$ state causes regeneration of the NO_3. Application of this procedure has greatly facilitated the study of the behavior of the NO_3 spectrum on isotopic substitution. It has also led to the first detection in absorption of the 366-cm^{-1} degenerate deformation fundamental of NO_3, including measurements of its isotopic shifts.[13]

Photoprocesses are also exceptionally important in stabilizing rare-gas-containing uncharged molecules, a process which will be considered in greater detail in other chapters of this volume. While most of these species do not possess unpaired electrons and technically are not free radicals, matrix isolation studies of these transient species have opened a new chapter in the chemistry of the rare gases. Typically, a deposit which contains suitable precursors is exposed to ultraviolet or vacuum ultraviolet radiation, followed by annealing, which results in the appearance or growth in infrared absorption of a HX^+Y^- product, where X is a rare-gas atom and Y a good electron captor, stabilized in the matrix by charge-transfer interaction. The first examples of these compounds were HXeCl, HXeBr, HXeI, and HKrCl, observed in krypton and xenon matrices by Pettersson and co-workers.[14] This work initiated an active program of research in that laboratory. A highlight in the study of this series of compounds was the stabilization and infrared study of HArF[15] and the subsequent discovery of the existence of a more stable trapping site for HArF in the argon matrix.[16] Compounds have also been studied in which the rare gas is coordinated with oxygen, sulfur, nitrogen, or carbon.[17,18]

3. Photoionization as a Source of Free Radicals and Molecular Ions

All of the photoprocesses discussed for neutral species can occur for molecular ions as well. The dependence of photoproducts on the wavelength of the irradiation becomes even more important with the extension of the energy range into the vacuum ultraviolet, necessary for ion production. This dependence is exemplified by a series of studies of the photolysis of $HCCl_3$. The 122-nm photolysis of $HCCl_3$ provided an excellent source of CCl_3.[19] However, a structured absorption at 1037 cm^{-1} was not readily assigned. With a compendium of ionization energies of small molecules[20] in hand, it was noted that the ionization energy of CCl_3 was 8.78 eV — a value that has since been revised downward to approximately 8.1 eV.[21,22] An updated online version of this compendium is currently available as the ion energetics portion of the *NIST Chemistry WebBook*, at http://webbook.nist.gov/chemistry/. When a 107-nm argon resonance lamp was substituted for the 122-nm radiation source, the cation product was instead $HCCl_2^+$.[23] The energy of the argon resonance lamp, 11.6 eV, slightly exceeds the 11.5-eV appearance energy of $HCCl_2^+$ from $HCCl_3$.[24,25]

3.1. *Discharge sampling*

Beginning in the early days of matrix isolation, many workers attempted to stabilize free radicals and molecular ions in inert matrices by passing the sample mixture through a discharge and rapidly quenching the products on the cryogenic observation surface. However, only a few simple, uncharged species were identified as a result of such experiments. Several important factors are responsible for this failure. Often, the energy released on quenching such mixtures exceeds the cooling capacity of the cell. Matrices are sufficiently rigid to inhibit molecular diffusion over only a relatively small temperature range. Diffusion becomes important at temperatures well below those at which the matrix material has a sufficient vapor pressure to be pumped away. A similar problem also occurred in the earliest studies of the vaporization of high-temperature samples. For such systems, the problem was readily solved by introducing the matrix gas downstream from the effusion cell. In addition, molecules introduced into the discharge region are extensively fragmented, resulting in mixtures in which atoms and exceptionally stable diatomics such as CN and CO predominate. Immediately after quenching, these atoms continue to diffuse and react.

3.2. *Modified discharge sampling*

A modified discharge sampling configuration, in which only the rare-gas matrix material is passed through the discharge and the molecule of interest mixed with a large excess of unexcited matrix gas is introduced downstream, has been much more successful for studies of the spectra of free radicals and molecular ions. In a recent study,[26] the yield of NH_4^+ trapped in a neon matrix was compared for various discharge configurations ranging from the conventional discharge of a Ne:NH_3 mixture during deposition to the codeposition of an undischarged Ne:H_2:NH_3 mixture with a beam of neon atoms that had been excited in a microwave discharge. By far the highest yield was obtained using the modified discharge configuration just described. Backstreaming into the discharge region is relatively unimportant in such experiments. Observations on many systems have demonstrated that the primary

photoionization processes are dominated by those which require energies near or below those of the first excited states of the rare gas. The infrared spectrum of the resulting deposit almost always includes prominent absorptions of the undecomposed molecule. The extent of excitation usually is insufficient for major occurrence of secondary photoprocesses.

When argon is chosen as the rare gas, the accessible ionization range is approximately 11.5–11.8 eV. This range is primarily useful for ionizing species which have relatively low ionization energies, such as halides, unsaturated molecules, and aromatic species. Nevertheless, such modified discharges through argon have been quite useful for free radical production, as in the use of acetylene as a source of HCC[27] and of methanol to form CH_2OH.[28]

When neon is chosen, the energy range which is most important for ion production is 16.61–16.84 eV. Two of the four neon-atom levels in that range readily emit radiation. The other two, the $^3P_0$ and $^3P_2$ levels, have calculated lifetimes of many seconds, and so can transfer energy to other species by forming a collision complex, which results in Penning ionization. The energy range provided by neon is sufficiently high to ionize virtually all molecules. Successful use of this configuration for electron spin resonance studies, which are highly sensitive to species with unpaired electrons, was first reported by Knight and Steadman.[29,30]

CO_2 was selected as the test molecule to check whether excited neon atoms produced with the modified discharge configuration could provide a sufficient yield of molecular ions for infrared detection.[31] The ionization energy of CO_2 is approximately 13.8 eV, and the gas-phase band center for its ν_3 fundamental had been determined to lie at 1423.01 cm^{-1}.[32] In the test experiment, the corresponding absorption appeared at 1421.7 cm^{-1}, and studies of isotopically enriched CO_2 were consistent with the CO_2^+ identification. Moreover, the ν_3 fundamental of CO_2^- was identified at 1658.3 cm^{-1}.

Because the rare-gas matrix may effectively remove excess energy from initially formed free radicals and molecular ions, processes which predominate in gas-phase photolysis systems sometimes may not occur in rare-gas matrices. An important example of this is provided by modified discharge sampling studies of allene and propyne.[33] The first ionization energy of allene, determined by molecular beam photoelectron

spectroscopy,[34] is 9.688(2) eV. Threshold photoelectron–photoion coincidence studies by Parr and co-workers[35] established thresholds and relative yields of cation products formed from allene at energies up to 20 eV. The appearance energy of $C_3H_3^+$ is 11.48(2) eV. At higher energies, that product grew rapidly, and was the predominant ion at 16.6 eV, although some allene cation, $C_3H_4^+$, persisted. Although the onset of $C_3H_2^+$ occurred at 13.5(2) eV, its yield grew slowly as the energy was increased. Similarly, the first ionization energy of propyne was determined to be 10.36 eV.[36] Threshold photoelectron–photoion coincidence studies[37] gave an appearance energy of $C_3H_3^+$ from propyne of 11.58(4) eV. At 16.6 eV, $C_3H_3^+$ was, once again, the most prominent cation, but appreciable $C_3H_4^+$ was still present. The most stable isomer of $C_3H_3^+$ was predicted to be the cyclic form, a prototypical aromatic molecule,[38,39] as was later confirmed.[40]

A modest amount of photoisomerization of allene to propyne and of propyne to allene was observed in the neon-matrix experiments using the modified discharge configuration. One set of absorptions was destroyed on irradiation of the initial deposit at wavelengths shorter than 280 nm, but persisted at somewhat shorter wavelengths when a small concentration of NO_2, a good electron captor, was added to the sample. This behavior is appropriate for a cation product. The positions of these absorptions did not correlate with those reported by Craig and co-workers[41] for polycrystalline salts of $C_3H_3^+$. Detailed isotopic substitution studies required the presence of four H atoms in the carrier molecule, which was identified as the allene cation. Calculations by Frenking and Schwarz[42] and by van der Hart[43] indicated that the potential energy surface for $C_3H_4^+$ has several minima, corresponding to the various stages in the photoisomerization of allene cation to propyne cation, as well as to the intermediate cation structures and to H-atom detachment to form *cyc*-$C_3H_3^+$. It was concluded that the lifetime of $C_3H_4^+$ is sufficiently long for collisions with the high concentration of neon atoms in the sampling region to remove the excess energy from the $C_3H_4^+$ before H-atom detachment can occur.

It sometimes happens that the ground-state structure of a cation differs from that of the corresponding uncharged molecule. For example, ionization of methyl fluoride results in the formation of H_2CFH^+, which

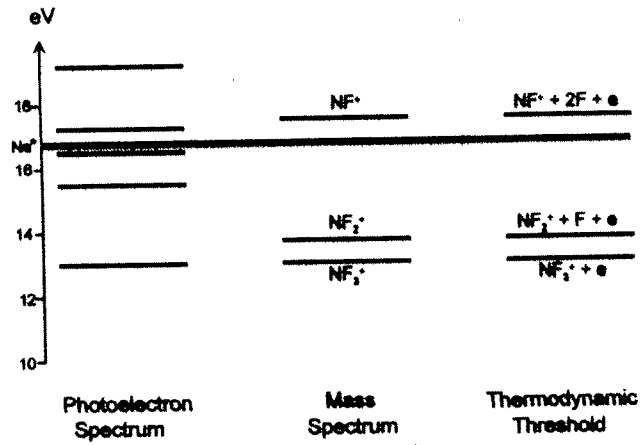

Fig. 1. Positions (eV) of the photoelectron bands of NF_3 and appearance energies (eV) of products of its photoionization.

is more stable than CH_3F^+. Such protonated species are known as ylidions. Although the methyl halide structure of the corresponding chloride and bromide is somewhat more stable than that of the ylidion, in matrix isolation experiments with the modified discharge configuration, the absorptions of both structures were present.[44]

3.3. *Secondary photolysis*

In many systems, secondary photolysis is exceptionally important for product identification. An excellent example of this generalization is provided by studies of NF_3.[45] Mass spectrometric studies by Dibeler and Walker obtained a first ionization energy of 13.00(2) eV for NF_3 and appearance energies of 14.12(1) and 17.54(2) eV for NF_2^+ and NF^+, respectively, derived from NF_3.[46] A later photoelectron–photoion coincidence study by Rüede and co-workers required downward revision of the appearance energy for NF_2^+ from NF_3 to 13.71(2) eV.[47] These observations indicate that, using the first group of excited states of the neon atom, between 16.61 and 16.84 eV, as the energy source, NF_2^+ can be produced but NF^+ is not accessible. This result is illustrated by Fig. 1.

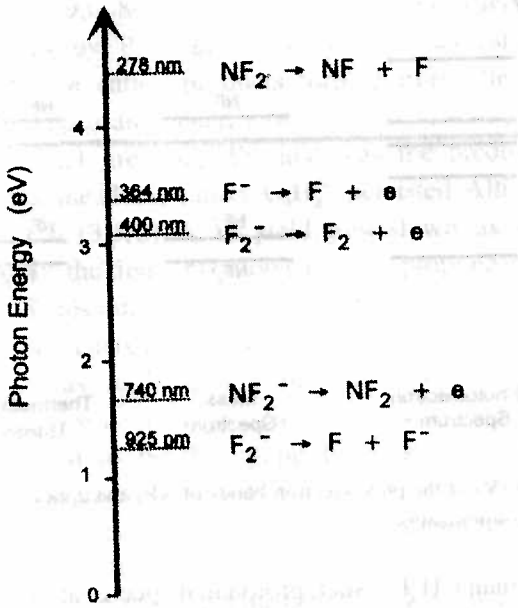

Fig. 2. Gas-phase photodissociation and photodetachment energies of the various anions expected to be formed in modified discharge experiments on Ne:NF_3 samples, together with the photodissociation energy of uncharged NF_2.

Jones and co-workers reported that the Penning ionization of NF_3 by Ne ($^3P_{0,2}$) atoms yielded 82% NF_2^+ and 18% NF_3^+.[48] Thus, the expected cation products in the modified discharge experiments on Ne:NF_3 samples are NF_2^+ and NF_3^+. The infrared spectrum of a Ne:NF_3 sample deposited without the discharge showed only the infrared absorptions of NF_3 and was unchanged on subsequent exposure of the deposit to filtered or unfiltered medium-pressure mercury-arc radiation. In contrast, infrared absorptions of uncharged NF_2 and of NF_2^+ and NF_3^+ were prominent in the spectra of Ne:NF_3 samples that had been codeposited with discharged neon.

As has been discussed in greater detail in a recent review by Jacox,[49] anions must also be present in the sample deposit in order to prevent the buildup of a high repulsive potential for the deposition of cations. Gas-phase studies of the interaction of low-energy electrons with NF_3 show that NF_3^- is no more than a minor product, but that the onset of

F^- and NF_2^- production occurs at very low electron energy.[50,51] The F^- atomic anions are relatively mobile, and can diffuse through the neon matrix and react with species trapped in the solid. The gas-phase photodissociation and photodetachment energies of the various anions expected to be present in this system are summarized, together with the photodissociation energy of uncharged NF_2, in Fig. 2. The onset of electron detachment from gas-phase NF_2^- occurs at 1.68(20) eV, which corresponds to the energy of approximately 740-nm photons.[50] Some of the F atoms can diffuse through the matrix during either the deposition or subsequent irradiations. These atoms may react to form F_2, which is immobile in the solid. F_2 is a good electron captor, with an electron affinity near 3.0 eV,[52,53] an energy which corresponds approximately to that of 400-nm radiation. The onset of electron detachment from any isolated F^- in the solid would occur at a slightly higher photon energy, corresponding to 364 nm.[54] Neon-matrix observations on many ion-production systems have shown that an excess electron energy of 1 or 2 eV is required for the detached electron to escape the site of its photoproduction.

The above generalizations receive further support from the results of anion observations for a Ne:NF_3:NO_2 = 1600:2:1 sample, shown in Fig. 3. Infrared absorptions of NF_2^-, as well as the familiar 1241.6-cm^{-1} absorption of NO_2^-, appeared in the initial deposit. At relatively low photon energies, the absorptions of NF_2^- decreased because of electron photodetachment, while the absorptions of uncharged NF_2 and of NO_2^-, which has a higher electron detachment threshold than does NF_2^-, grew. At higher photon energies, the NO_2^- absorption also decreased, and the NF_2 absorptions grew considerably more.

The technique has since been useful for studying molecules with very high first ionization energies. Kickel and co-workers estimated the first ionization energy of SiF_4 to be 15.29(3) eV.[55] Ionization of that molecule has a slow onset, with SiF_3^+ the predominant product both in the gas phase and in a neon matrix.[56] BF_3 has an even higher first ionization energy, 15.55(4) eV, with the appearance energy of BF_2^+ from BF_3 only slightly higher, 15.81 eV.[57] Above that energy, BF_2^+ is the predominant ion product. The spectrum of the initial sample deposit included absorptions of all three vibrational fundamentals and a combination band

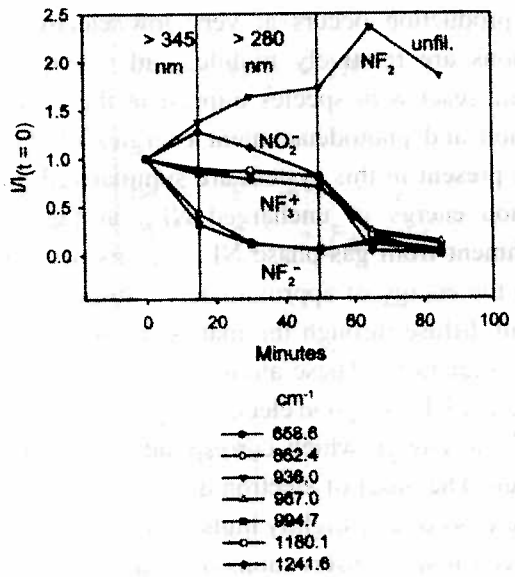

Fig. 3. Fractional changes in the intensities of various product absorptions observed in a modified discharge sampling experiment on an $Ne:NF_3:NO_2$ = 1600:2:1 experiment after subsequent irradiation with various wavelength ranges of the output of a medium-pressure mercury-arc lamp.

of BF_2.[58] Although absorptions of BF_2^+ were identified in the product spectrum, BF^+ was not, and BF was at most a minor contributor. Other product absorptions appeared, including several which had a disappearance threshold near 780 nm. The positions of this set of absorptions are appropriate for their contribution by BF_3^-. It is inferred that the electron affinity of BF_3, which has not been definitively established, has its upper bound at an energy corresponding to approximately 780 nm.

3.4. *Ion–matrix interaction*

As has been considered in greater detail in a recent review of the products of ion–molecule reactions in matrices,[49] many small molecular ions have exceptionally high reactivities. Indeed, the probability of their

reaction on collision with another species often approaches unity. In contrast, the corresponding collisional reaction probability for a free radical–molecule pair is typically two or three orders of magnitude smaller. Often collisions of an ion with its uncharged counterpart lead to the stabilization of dimer ions in the matrix. Indeed, in studies on Ne:NO samples the trimer anion also contributes prominent absorptions to the spectrum.[59]

The exceptionally high reactivity of molecular ions extends to the occurrence of significant interaction with rare-gas matrices, accompanied by matrix shifts which may be as great as several hundred cm^{-1}. Several matrix properties need to be considered in order to minimize ion–matrix interactions. The most important of these are compared for inert solid rare gas and diatomic molecule matrices in Fig. 4. Because of the recent availability of helium cluster studies, helium is also included in the comparison. A high ionization energy of the matrix species reduces the extent of its charge-transfer interaction with molecular ions, which is greatest when the difference between the ionization energy of the molecule and that of the matrix is small. Almost all small molecules have first ionization energies below 16 eV. Neon has a significantly higher ionization energy than any of the other solid matrix materials. The low polarizabilities of helium and neon also suggest that they should have minimal interaction with highly polar ionic species. Proton sharing is an important cause of the large matrix shifts observed for proton stretching fundamentals of a number of protonated cations in rare-gas and molecular complexes and in matrices. Helium and neon, which have appreciably smaller proton affinities than those of most molecules,[60] excel in minimizing the importance of proton sharing, as well. Because the proton affinity of helium is only slightly smaller than that of neon, proton sharing may cause significant spectral shifts in both helium clusters and neon matrices for some protonated species derived from molecules which have relatively low proton affinities.

In 1972, Bondybey and Pimentel noted the appearance of infrared absorptions in their discharge sampling experiments using argon or krypton as the matrix material which they attributed to the trapping of interstitial hydrogen atoms.[61] The origin of the relatively high absorption intensities attributed to these interstitial atoms remained puzzling. The

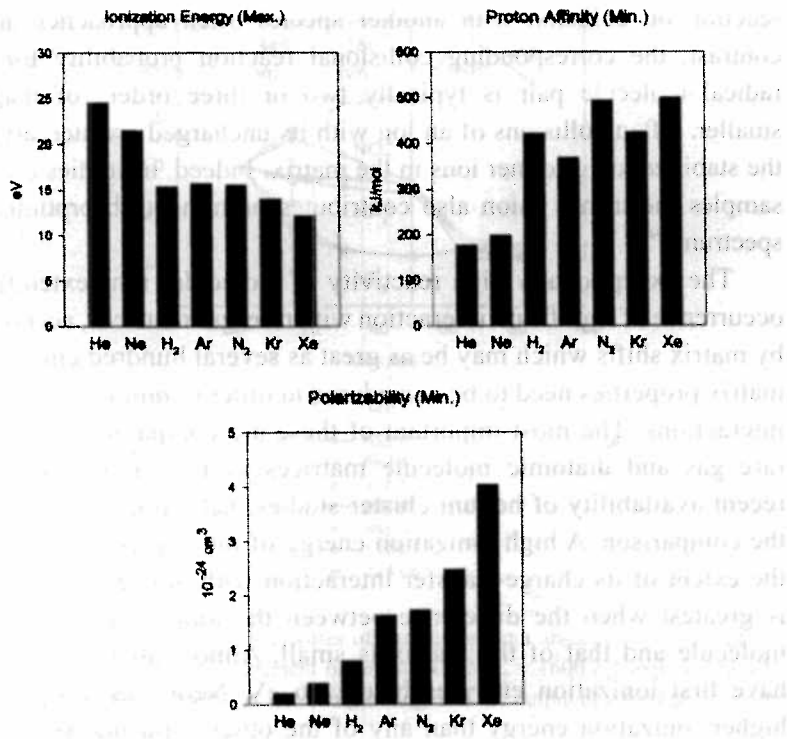

Fig. 4. Matrix properties needed to minimize ion–matrix interactions.

following year, Milligan and Jacox noted that these same absorptions had been seen in many of their 122-nm photolysis studies on matrix isolation systems which had in common the presence of an H-atom source and an atom or group of atoms that was a good electron captor and proposed their reassignment to HAr_n^+ and HKr_n^+, with $n = 2$, 4, or 6.[62] (Later studies favored $n = 2$.) In support of this reassignment, they cited flowing afterglow reaction tube observations on the argon–hydrogen system which indicated that HAr_2^+ was a dominant cation, as well as a mass spectrometric study by Chupka and Russell in which ArH^+ was demonstrated to be formed by the reaction of an Ar atom with an H atom excited to its $2\ ^2S$ state, at 122 nm.[63] Clustering of that species with one or more additional Ar atoms in the solid would occur readily.

In an argon-matrix discharge sampling study of $HCCl_3$, Jacox observed prominent infrared absorptions of $HCCl_2^+$.[64] The photodestruction threshold of that species was near 280 nm. When the photolyzing radiation had a wavelength cutoff shorter than 260 nm, a marked increase in the concentration of HAr_2^+ resulted, which is consistent with the calculated threshold energy for proton transfer from $HCCl_2^+$ to the argon matrix. Similar experiments using a krypton matrix, in which HKr_2^+ appeared, were consistent with this mechanism. Studies which support the identification of HAr_2^+ and HKr_2^+ and extend our information on their properties have since been conducted in a number of laboratories.[65–68]

As discussed in a review by Bieske and Dopfer,[69] many protonated species form complexes with rare-gas atoms. This complexation usually results in a significant shift in the position of the fundamental contributed by the proton stretching vibration of MH^+. The magnitude of this shift depends on the difference between the proton affinity of the parent molecule, M, and that of the rare gas. The dependence on the nature of the rare-gas atom in the complex is exemplified by a series of gas-phase observations on the CH stretching fundamental of HCO^+. In its complex with a single helium atom[70] (proton affinity 177.8 kJ mol^{-1}), this fundamental appears 12.4 cm^{-1} below the gas-phase band center. For a neon atom (proton affinity 198.8 kJ mol^{-1}),[71] the shift is 42.6 cm^{-1}; for an argon atom (proton affinity 369.2 kJ mol^{-1}),[72] the shift is 273.7 cm^{-1}; and for a hydrogen molecule (proton affinity 422.3 kJ mol^{-1})[73] the shift is 249 cm^{-1}. Two proton affinities, 594 kJ mol^{-1} for complexation at the C atom and 426.3 kJ mol^{-1} for complexation at the O atom, have been reported for carbon monoxide. Correspondingly, spectra have been observed for both HCO^+ and HOC^+. All proton affinities here cited are values given by Hunter and Lias.[60]

The extent of the shift resulting from complexation of a rare gas with a protonated molecule is dependent on the number of rare-gas atoms in the complex. A detailed study for gas-phase Ar_nHCO^+ clusters, which have values of n from 1 to 13, has been made by Nizkorodov and co-workers.[72]

The proton affinity of the F atom is exceptionally low, 340.1 kJ mol^{-1}.[60] This value approaches that of the neon atom, suggesting that

there should be a strong interaction between HF^+ and the neon atom or matrix. In an attempt to stabilize HF^+ in a neon matrix, Lugez and co-workers[74] found a shift of approximately 700 cm^{-1} for the HF^+ stretching fundamental, suggesting that the absorption was best characterized as a proton stretching vibration of $NeHF^+$.

If only cations (or anions) were to be deposited in a matrix, a high electric field would rapidly be established that would repel ions of the same sign from the deposition surface. In practice, processes such as electron flow into the deposit may occur to relieve the charge imbalance. A more detailed discussion of this phenomenon is given in a recent review.[49]

3.5. *Stabilization of anions*

The 122-nm photolysis of acetylene in rare-gas matrices proved to be an excellent source of both HCC and C_2, which was stabilized in its ground singlet state.[75] Still other absorptions in the visible spectral region that had previously been attributed to the Swan bands of triplet C_2 also appeared. These bands had vibrational spacings which differed appreciably from those measured for the Swan bands of gas-phase C_2. Subsequently, the bands were reassigned to C_2^-, formed by electron capture.[76] C_2 has an exceptionally high electron affinity, 3.27 eV.[77] The source of the photoelectrons still has not been definitively identified. One possibility is photoionization of a low-ionization-energy species such as diacetylene, the product of combination of pairs of HCC radicals formed in the intense beam of 122-nm radiation. The identification was confirmed by other experiments in which cesium atoms were added to the sample during the initial deposition, with concurrent 122-nm irradiation. Cesium has an exceptionally low ionization energy and provides a supplementary source of electrons. Fortunately, the density of the Rydberg states of C_2H_2 near 122 nm was sufficiently low to permit photoproduction of appreciable C_2. The yield of C_2^- increased greatly. Further details of the C_2^- identification are given in a recent review.[78]

That experiment demonstrated that anions can be stabilized in rare-gas matrices and paved the way for many subsequent anion identifications. Alkali metal atoms were adopted as a convenient source

of electrons. The first subsequent anion identification was that of NO_2^-.[79,80] The electron affinity of NO_2, 2.273(5) eV,[81] is sufficiently high that charge-transfer interaction with the alkali metal occurs during the deposition. Often spontaneous charge-transfer interaction occurs during the codeposition of an alkali metal with another species. The electron affinity of SO_2 is 1.10 eV.[82,83] Although in the argon-matrix experiments all three vibrational fundamentals of SO_2^- were identified in the initial deposit,[84] subsequent experiments by Bencivenni and co-workers[85] provided evidence that the product was $M^+SO_2^-$, with M^+ the alkali metal cation. The problem was later avoided in experiments on a $Ne:SO_2$ sample using the modified discharge configuration.[86] Unlike the cations formed from alkali metal atoms, SO_2^+ cannot migrate through the matrix and form a complex with SO_2^-. In this experiment, the ν_3 fundamental of SO_2^- was shifted upward by approximately 50 cm^{-1}. Even when alkali metal atoms are codeposited with CO_2, which has an adiabatic electron affinity of –0.6 eV,[87] in an argon matrix absorptions attributed to the anion appeared.[88] In that study a new absorption attributed to CO_2^- appeared near 1600 cm^{-1}, at a position that was somewhat dependent on the alkali metal used in the experiment. The participation of the alkali metal in a complex with CO_2^- was confirmed by a modified discharge sampling experiment on a Ne: CO_2 mixture.[31] The ν_3 fundamental of CO_2^- was identified at 1658.3 cm^{-1} in the resulting neon-matrix deposit. The absorption is readily destroyed by subjecting the deposit to visible radiation. CO_2^+ is also stabilized in this system, but cannot migrate through the neon lattice.

In other experiments, an $Ar:N_2O$ mixture was codeposited with a beam of alkali metal atoms.[80] Although new absorptions did not appear in the initial deposit, when the deposit was exposed to the full or filtered radiation of a medium-pressure mercury arc, the absorptions of N_2O gradually decreased in intensity and a prominent new absorption appeared at 1206 cm^{-1}. On prolonged irradiation this absorption was also destroyed, and the NO stretching absorptions of $(NO)_2$ grew in intensity. Isotopic substitution absorption studies supported the assignment of the new absorption to $N{=}NO_2^-$, produced from the addition of O^- to N_2O.

In 1968, Noble and Pimentel observed absorptions near 700 and 960 cm^{-1} which they attributed to an uncharged ClHCl species trapped in an

Ar:HCl sample that had been passed through a glow discharge while it was being deposited.[89] Subsequently, Milligan and Jacox observed the same two peaks with greatly enhanced intensity in the infrared spectrum of an Ar:HCl mixture that had been codeposited with a beam of potassium atoms and then exposed to 254-nm radiation.[90] This observation dictated the reassignment of the two absorptions to the $ClHCl^-$ anion. The reassignment has stood the test of time. Shortly thereafter, Bondybey and co-workers repeated the glow discharge sampling experiment using an Ar:HBr mixture and attributed two new absorptions to uncharged BrHBr.[91] However, this pair of peaks was reproduced when an Ar:HBr mixture was codeposited with a beam of alkali metal atoms and then subjected to 254-nm irradiation.[92] Coulombic interaction resulting from charge transfer facilitates anion formation when an alkali metal is present in the system. A more detailed discussion of the role of charge transfer has been given by Jacox.[93]

The stabilization of $N{=}NO_2^-$ suggested that the codeposition of an $Ar{:}CO_2{:}N_2O$ mixture with an alkali metal and subsequent mercury-arc irradiation might lead to the appearance of the important CO_3^- free radical, which is isoelectronic with $N{=}NO_2^-$. Two new CO stretching absorptions appeared in the resulting experiment. Other experiments with similar results were conducted starting instead with an $Ar{:}CO{:}O_2$ mixture.[94] However, the appearance of two appreciably separated CO stretching absorptions was at first puzzling, since CO_3^- was expected to possess D_{3h} symmetry, for which only a single, doubly degenerate CO stretching fundamental should be infrared-active. It was suggested that the apparent anion structure was distorted because of the inhomogeneous electric field associated with the alkali metal atomic cations. The argument was supported by observations on the stabilization of $M^+NO_3^-$ in matrices. Although X-ray diffraction studies had definitively established that the nitrate anion in crystalline alkali metal nitrates possesses threefold symmetry, Smith and co-workers[95] reported a splitting of similar magnitude for the degenerate NO stretching fundamental of vapors from various alkali metal nitrates trapped in inert matrices. A later neon-matrix study involving the codeposition of a $Ne{:}NO_2{:}O_2$ or a $Ne{:}NO{:}O_2$ sample with a beam of neon atoms that had been excited in a microwave discharge led to the appearance of a single

prominent NO stretching absorption of NO_3^- trapped in solid neon.[96] In these experiments, molecular cations were trapped throughout the solid, providing a more homogeneous electric field than for atomic cations, which could diffuse through the lattice to sites near the molecular anions.

The possibility of electron capture in studies on ionic systems increases the number of processes which may occur. The activation barrier for electron diffusion through rare-gas matrices is low. Because electron–cation recombination is highly exothermic, the uncharged product may contribute prominent absorptions to the spectrum. In addition to the expected anion, typically impurities such as CO_2 and O_2 which are always present in low concentration provide weak electron traps. Sometimes an electron that is photodetached from a weak electron trap is captured by another species having a higher electron affinity, as exemplified by the previous discussion of the $Ne{:}NF_3{:}NO_2$ system.

If photodestruction of cations results from electron capture rather than from photodecomposition, the threshold and extent of cation photodestruction will depend on the properties of the anions in the system.[49] When electrons are released from weak electron traps by exposure of the sample to low-energy radiation, a fraction of the cations will be neutralized by electron capture. On prolonged irradiation, the electron source is depleted, and the concentration of cations levels off at a new, lower value. When a somewhat more energetic radiation source is used, electrons are released from slightly stronger electron traps, and the concentration of cations "tails off" at a new, lower value. Such behavior can aid in determining that a species is a cation. Addition of a good electron captor (e.g., Cl_2, NO_2) to the system may increase the energy range of stability of cations, facilitating their observation and identification. However, when such a species is added to the sample it is necessary to consider the possibility of reaction of the added species or one of its photodissociation products with other atoms or molecules in the system.

4. Summary

Photodecomposition of a free radical precursor trapped in a rare-gas matrix proceeds in the same spectral region and usually yields the same

products as observed in the gas phase. However, when the energy barrier to the reverse process is low, cage recombination in the matrix suppresses product formation. Alternatively, cage recombination may result in isomerization. Occasionally, the product observed in gas-phase studies results from dissociation of an initially formed excited species. When this occurs, the matrix may collisionally deactivate the initially formed species before there is sufficient time for it to rearrange or dissociate. When photodecomposition eliminates an atom from the precursor, atomic diffusion through the solid can result in stabilization of the free radical formed by the atom detachment. The released atom sometimes reacts with another species to form a second free radical product.

Similar principles apply to the stabilization of molecular ions in rare-gas matrices, with the added generalization that electrons, like atoms, have at least limited mobility in the matrix. In ionic systems, approximate charge neutrality of the deposit must be maintained. Small molecular ions are often much more reactive than are free radicals, and may quite strongly interact even with the matrix atoms.

In studying the spectra of both free radicals and molecular ions trapped in rare-gas matrices, reference to the literature for the corresponding gas-phase processes defines energetic constraints on the system and aids greatly in selecting wavelength ranges for the study of secondary photoprocesses.

References

1. D. E. Milligan, *J. Chem. Phys.* **35**, 372 (1961).
2. D. E. Milligan, *J. Chem. Phys.* **35**, 1491 (1961).
3. C. B. Moore and G. C. Pimentel, *J. Chem. Phys.* **41**, 3504 (1964).
4. M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **40**, 2457 (1964).
5. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **38**, 2627 (1963).
6. P. Warneck, *Appl. Opt.* **1**, 721 (1962).
7. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **43**, 4487 (1965).
8. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47**, 5146 (1967).
9. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47**, 5157 (1967).
10. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47**, 278 (1967).
11. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **51**, 277 (1969).

12. M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **129**, 204306 (2008).
13. H. Beckers, H. Willner and M. E. Jacox, *ChemPhysChem.* **10**, 706 (2009).
14. M. Pettersson, J. Lundell and M. Räsänen, *J. Chem. Phys.* **102**, 6423 (1995).
15. L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell and M. Räsänen, *Nature* **406**, 874 (2000).
16. L. Khriachtchev, M. Pettersson, A. Lignell and M. Räsänen, *J. Am. Chem. Soc.* **123**, 8610 (2001).
17. M. Pettersson, J. Lundell and M. Räsänen, *Eur. J. Inorg. Chem.*, 729 (1999).
18. L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen and M. Räsänen, *J. Am. Chem. Soc.* **125**, 4696 (2003).
19. E. E. Rogers, S. Abramowitz, M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **52**, 2198 (1970).
20. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*, National Bureau of Standards,Washington, DC (1969).
21. J. W. Hudgens, R. D. Johnson III, R. S. Timonen, J. Seetula and D. Gutman, *J. Phys. Chem.* **95**, 4400 (1991).
22. E. S. J. Robles and P. Chen, *J. Phys. Chem.* **98**, 6919 (1994).
23. M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **54**, 3935 (1971).
24. A. S. Werner, B. P. Tsai and T. Baer, *J. Chem. Phys.* **60**, 3650 (1974).
25. J. L. Holmes, F. P. Lossing and R. A. McFarlane, *Int. J. Mass Spectrom. Ion Proc.* **86**, 209 (1988).
26. M. E. Jacox and W. E. Thompson, *Phys. Chem. Chem. Phys.* **7**, 768 (2005).
27. M. E. Jacox and W. B. Olson, *J. Chem. Phys.* **86**, 3134 (1987).
28. M. E. Jacox, *Chem. Phys.* **59**, 213 (1981).
29. L. B. Knight Jr. and J. Steadman, *J. Chem. Phys.* **77**, 1750 (1982).
30. L. B. Knight Jr., *Acc. Chem. Res.* **19**, 313 (1986).
31. M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **91**, 1410 (1989).
32. K. Kawaguchi, C. Yamada and E. Hirota, *J. Chem. Phys.* **82**, 1174 (1985).
33. D. Forney, M. E. Jacox, C. L. Lugez and W. E. Thompson, *J. Chem. Phys.* **115**, 8418 (2001).
34. Z. Z. Yang, L. S. Wang, Y. T. Lee, D. A. Shirley, S. Y. Huang and W. A. Lester Jr., *Chem. Phys. Lett.* **171**, 9 (1990).
35. A. C. Parr, A. J. Jason and R. Stockbauer, Int. *J. Mass Spectrom. Ion Proc.* **26**, 23 (1978).
36. T. Nakayama and K. Watanabe, *J. Chem. Phys.* **40**, 558 (1964).
37. A. C. Parr, A. J. Jason, R. Stockbauer and K. E. McCulloh, *Int. J. Mass Spectrom. Ion Proc.* **30**, 319 (1979).
38. J. D. Roberts, A. Streitweiser and C. M. Regan, *J. Am. Chem. Soc.* **74**, 4579 (1952).
39. F. P. Lossing, *Can. J. Chem.* **50**, 3973 (1972).
40. J. L. Holmes and F. P. Lossing, *Can. J. Chem.* **57**, 249 (1979).

41. N. C. Craig, J. Pranata, S. J. Reinganum, J. R. Sprague and P. S. Stevens, *J. Am. Chem. Soc.* **108**, 4378 (1986).
42. G. Frenking and H. Schwarz, *Int. J. Mass Spectrom. Ion Phys.* **52**, 131 (1983).
43. W. J. van der Hart, *Int. J. Mass Spectrom. Ion Proc.* **151**, 27 (1995).
44. C. L. Lugez, D. Forney, M. E. Jacox and K. K. Irikura, *J. Chem. Phys.* **106**, 489 (1997).
45. M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **102**, 6 (1995).
46. V. H. Dibeler and J. A. Walker, *Inorg. Chem.* **8**, 1728 (1969).
47. R. Rüede, H. Troxler, C. Beglinger and M. Jungen, *Chem. Phys. Lett.* **203**, 477 (1993).
48. M. T. Jones, T. D. Dreiling, D. W. Setser and R. N. McDonald, *J. Phys. Chem.* **89**, 4501 (1985).
49. M. E. Jacox, *Int. J. Mass Spectrom.* **267**, 268 (2007).
50. P. W. Harland and J. L. Franklin, *J. Chem. Phys.* **61**, 1621 (1974).
51. G. D. Sides and T. O. Tiernan, *J. Chem. Phys.* **67**, 2382 (1977).
52. J. A. Ayala, W. E. Wentworth and E. C. M. Chen, *J. Phys. Chem.* **85**, 768 (1981).
53. P. G. Wenthold and R. R. Squires, *J. Phys. Chem.* **99**, 2002 (1995).
54. C. Blondel, P. Cacciani, C. Delsart and R. Trainham, *Phys. Rev.* **A40**, 3698 (1989).
55. B. L. Kickel, E. R. Fisher and P. B. Armentrout, *J. Phys. Chem.* **97**, 10198 (1993).
56. M. E. Jacox, K. K. Irikura and W. E. Thompson, *J. Chem. Phys.* **103**, 5308 (1995).
57. V. H. Dibeler and S. K. Liston, *Inorg. Chem.* **7**, 1742 (1968).
58. M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* **102**, 4747 (1995).
59. C. L. Lugez, W. E. Thompson, M. E. Jacox, A. Snis and I. Panas, *J. Chem. Phys.* **110**, 10345 (1999).
60. E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data* **27**, 413 (1998).
61. V. E. Bondybey and G. C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
62. D. E. Milligan and M. E. Jacox, *J. Mol. Spectrosc.* **46**, 460 (1973).
63. W. A. Chupka and M. E. Russell, *J. Chem. Phys.* **49**, 5426 (1968).
64. M. E. Jacox, *Chem. Phys.* **12**, 51 (1976).
65. C. A. Wight, B. S. Ault and L. Andrews, *J. Chem. Phys.* **65**, 1244 (1976).
66. H. M. Kunttu and J. A. Seetula, *Chem. Phys.* **189**, 273 (1994).
67. N. Legay-Sommaire and F. Legay, *Chem. Phys. Lett.* **314**, 40 (1999).
68. T. D. Fridgen, X. K. Zhang, J. M. Parnis and R. E. March, *J. Phys. Chem.* **A104**, 3487 (2000).
69. E. J. Bieske and O. Dopfer, *Chem. Rev.* **100**, 3963 (2000).
70. S. A. Nizkorodov, J. P. Maier and E. J. Bieske, *J. Chem. Phys.* **103**, 1297 (1995).
71. S. A. Nizkorodov, O. Dopfer, M. Meuwly, J. P. Maier and E. J. Bieske, *J. Chem. Phys.* **105**, 1770 (1996).
72. S. A. Nizkorodov, O. Dopfer, T. Ruchti, M. Meuwly, J. P. Maier and E. J. Bieske, *J. Phys. Chem.* **99**, 17118 (1995).
73. E. J. Bieske, S. A. Nizkorodov, J. E. Bennett and J. P. Maier, *J. Chem. Phys.* **102**, 5152 (1995).

74. C. L. Lugez, M. E. Jacox and R. D. Johnson III, *J. Chem. Phys.* **110**, 5037 (1999).
75. D. E. Milligan, M. E. Jacox and L. Abouaf-Marguin, *J. Chem. Phys.* **46**, 4562 (1967).
76. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **51**, 1952 (1969).
77. D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos and D. M. Neumark, *J. Chem. Phys.* **95**, 8753 (1991).
78. M. E. Jacox, *Acc. Chem. Res.* **37**, 727 (2004).
79. D. E. Milligan, M. E. Jacox and W. A. Guillory, *J. Chem. Phys.* **52**, 3864 (1970).
80. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **55**, 3404 (1971).
81. K. M. Ervin, J. Ho and W. C. Lineberger, *J. Phys. Chem.* **92**, 5405 (1988).
82. R. J. Celotta, R. A. Bennett and J. L. Hall, *J. Chem. Phys.* **60**, 1740 (1974).
83. M. R. Nimlos and G. B. Ellison, *J. Phys. Chem.* **90**, 2574 (1986).
84. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **55**, 1003 (1971).
85. L. Bencivenni, F. Ramondo, R. Teghil and M. Pelino, *Inorg. Chim. Acta* **121**, 207 (1986).
86. D. Forney, C. B. Kellogg, W. E. Thompson and M. E. Jacox, *J. Chem. Phys.* **113**, 86 (2000).
87. M. Knapp, O. Echt, D. Kreisle, T. D. Märk and E. Recknagel, *Chem. Phys. Lett.* **126**, 225 (1986).
88. M. E. Jacox and D. E. Milligan, *Chem. Phys. Lett.* **28**, 163 (1974).
89. P. N. Noble and G. C. Pimentel, *J. Chem. Phys.* **49**, 3165 (1968).
90. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **53**, 2034 (1970).
91. V. Bondybey, G. C. Pimentel and P. N. Noble, *J. Chem. Phys.* **55**, 540 (1971).
92. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **55**, 2550 (1971).
93. M. E. Jacox, *Rev. Chem. Intermed.* **2**, 1 (1978).
94. M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.* **52**, 363 (1974).
95. D. Smith, D. W. James and J. P. Devlin, *J. Chem. Phys.* **54**, 4437 (1971).
96. D. Forney, W. E. Thompson and M. E. Jacox, *J. Chem. Phys.* **99**, 7393 (1993).