The infrared spectroscopy of the products of ion–molecule reactions trapped in the solid rare gases

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Abstract

Studies of the infrared spectra of small molecular ions offer valuable information regarding the structures and chemical bonding properties of these species. Suitable concentrations of ions for such studies can be obtained by trapping them in dilute solution in a rare-gas solid. The characteristics of infrared absorptions of species trapped in the various rare gases are surveyed, as are factors important in ion production and identification. Emphasis is given to the development and application of a modified discharge configuration which has permitted the identification of many small molecular cations and anions. This configuration is now also being used for studies of the infrared spectra of primary products of some ion–molecule reactions.
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1. Introduction

Although mass spectrometry excels at determining the composition and reaction rates of molecular ions, molecular spectroscopy has much to contribute to our knowledge of their structures and energy levels. The familiar assumption that the ground-state vibrational energy levels of ions are similar to those of the parent neutral is not always valid. For example, CO_2^+ and CO_2 are linear, but CO_2^- is bent. The antisymmetric stretching fundamentals of these three species lie at 1423.08, 2349.16, and 1658.3 cm^{-1}, respectively.

Infrared spectroscopy is a valuable ally to photoelectron and electronic spectroscopy for probing the molecular properties of reaction intermediates. All molecules except homonuclear diatomics have infrared absorptions. The selection rules for infrared and these other spectroscopies differ; the pattern of ground-state molecular energy levels of a given molecule can be more completely characterized when both electronic spectral observations and infrared observations are available. Vibrational transitions usually occur in spectral regions characteristic of specific types of bonding. Analysis of the ground-state vibrational

energy level pattern permits identification of isomers and gives detailed information about the types and strengths of the chemical bonds. For moderate-size molecules, detailed analysis of the rotational structure in the gas-phase spectrum may yield a quantitative determination of the molecular structure. For species with incompletely filled low-lying molecular orbitals, experimentally determined structures and energy level data are potentially very important aids to refinement of the approximations used in ab initio calculations of molecular properties.

Small molecular ions provide the ultimate challenge to the spectroscopist, as they often have appreciable probabilities for reaction on each collision with a reaction partner. Even when there is an initial rapid burst in the production of these species, they are used up too quickly to permit detection by any but the most responsive and sensitive techniques. Since about 1980, the application of new spectroscopic tools and techniques such as diode laser absorptions and laser difference frequency spectroscopy has yielded high resolution infrared spectroscopic data for specific vibrational bands of a number of important small free radicals and molecular ions. Among the first of these was H_3^+, for which the infrared spectrum was identified and has since been extensively studied in the laboratory of Oka, who has published an account of its discovery [1].

Matrix isolation sampling provides a widely applicable tool to circumvent the problem posed by the extremely great reactivity

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of ions. Whittle et al. [2] proposed that, because nitrogen and the rare gases are usually chemically inert and are transparent from the far infrared well into the vacuum ultraviolet, dilute solid solutions of reaction intermediates in these materials could be used to study both their infrared and optical spectra. Early experiments confirmed that these solids are sufficiently rigid to effectively inhibit molecular diffusion. Vibrational and electronic energy level data for almost 4000 short-lived neutral and ionic reaction intermediates which contain from 3 to 16 atoms, obtained both in the gas phase and in inert solid matrices, are now available and are the subject of a series of recent reviews [3–5], and of a computer-searchable database, a part of the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/). That database includes vibrational and electronic spectral data resulting from gas phase and matrix isolation observations for more than 700 cations and 500 anions. Merged data from the exceptionally important published databases concerned with various aspects of ion energetics which were developed and extended for many years by Sharon Lias are also a major part of the ion energetics database contributed by Sharon G. Lias and John E. Bartmess to that same website.

The great reactivity of many small molecular ions has made possible the stabilization in solid neon not only of the initially formed ion but also of some of its primary reaction products with other species. This paper reviews the application of matrix isolation spectroscopy to studies of the infrared spectra of small molecular ions, with emphasis on these ion–molecule reaction products.

2. Properties of matrix-isolated samples

Because of the very low temperature of the deposit, species formed in excited states are quenched to their ground state or, for a few simple hydrides, to the rotational distribution characteristic of the observation temperature. Molecules are trapped in one or two major sites in the solid. Typical half widths of infrared absorptions of adequately isolated molecules are less than $1 \, cm^{-1}$, with splittings of only a few cm^{-1} between contributions from different trapping sites. These conditions are favorable for the study of isotopic shifts, which provide an extremely important tool for positive product identifications and for structure determination.

Shifts of typical infrared absorptions of species trapped in rare gas or nitrogen matrices from the corresponding gas-phase band centers have been surveyed for the ground-state vibrational energy levels of diatomic molecules [6,7] and short-lived diatomic and polyatomic species [7,8]. The fundamental absorptions of most species isolated in argon matrix lie within 1% of the gas-phase band centers, and very few deviate by more than 2%. The heavier rare gases and nitrogen show somewhat larger matrix shifts.

Electron correlation is important for species which possess one or more unpaired electrons. Consequently, obtaining physically realistic results for these species from ab initio and density functional calculations presents a much greater challenge than for most ordinary molecules. Byrd et al. [9] compared the results of a number of frequently used "package" calculations

of ground-state structures and vibrational fundamentals of free radicals with the experimentally determined values. Hartree-Fock calculations showed unacceptably large deviations, and the results of MP2 calculations were erratic. The smallest vibrational frequency deviations resulted from CCSD, CCSD(T), and B3LYP calculations. These deviations were compared by Jacox [7] with the deviations from the gas-phase band centers observed in neon- and argon-matrix studies of the same molecules. Even when relatively large basis sets were used, the calculated deviations were several times as great as those characteristic of the matrix observations. More sophisticated calculations can, of course, improve the agreement with experiment, but there remains much room for both further experimental studies and refinement of calculational procedures. Dialogue between experimentalists and theoreticians promises to be mutually beneficial.

Observation of a large number of matrix isolation systems supports the generalization that in neon and argon matrices atoms can diffuse to at least a limited extent, whereas even small molecules are effectively trapped. Atoms can also undergo cage recombination with a molecular fragment at the site of their photoproduction, sometimes resulting in the stabilization of an isomer of the original molecule. Where photodissociation of a precursor results in the formation of a pair of molecules trapped in adjacent sites, stabilization of the fragment molecules occurs only if the activation energy for the reverse recombination is large. Isomerization sometimes also results from recombination of the fragment molecules.

3. Production and properties of molecular ions

3.1. Strategies for ion identification

Isotopic substitution is the "gold standard" for ion identification in both gas phase and matrix isolation studies. In the gas phase, it enlarges the number of rotational constants available for structure determination. In the matrix, the isotopic shifts give information on the extent of participation of the isotopically substituted atom in each of the observed vibrational absorptions, greatly aiding the vibrational assignment.

Photolysis of the initial deposit by filtered radiation permits the product absorptions to be sorted by photolysis threshold, aiding in the initial product identification.

While ab initio and density functional calculations are often extremely helpful, some cautions must be noted. Although coincidence of the calculated absorption pattern with the observed spectrum is very helpful in product identification, it is not *sufficient* for a positive identification. Problems are especially likely to be encountered for species with similar elemental composition but somewhat different numbers of atoms and with isomers which have quite similar types of chemical bonds. This complication is exemplified by a recent study of the ions produced in modified discharge sampling experiments on allene and methylacetylene [10]. Comparison of the observed and calculated isotopic shift patterns greatly enhances the power of computational chemistry for positive spectral identifications.

3.1.1. Mass selection

In recent years, a number of laboratories have conducted matrix isolation studies on mass-selected beams. These experiments have been very useful for simplifying the composition of the system, but less useful for isolating individual charged species. The first mass selection study, by Forney et al. [11], used an exceptionally sensitive detection configuration and yielded electronic absorptions of C_2^+, $NCCN^+$, and $ClCCCl^+$ trapped in a neon matrix. Later, Halasinski et al. reported the infrared detection of the ν_3 fundamental of matrix-isolated CF_3^+ [12], as well as the infrared detection of ν_3 of CS_2^+ and CS_2^- [13]. If only cations or anions are deposited, in a very short time a high repulsive potential to further ion deposition develops, and other processes occur which lead to approximate charge neutrality of the overall deposit. The Maier group detected flow of electric current in the system. Possible complications beyond the mass selection stage, such as fragmentation and reaction with H_2O and other impurities desorbed from the walls of the system during the several hours usually needed for sample deposition, must always be considered. Leroi and co-workers [14] 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 the cation signals, as well as the infrared absorption of CO_2^-, by adding a small amount of CO_2 to the matrix gas.

3.1.2. Distinguishing cations from anions

Distinguishing a cation from an anion of the same chemical formula in a matrix isolation experiment is straightforward when the corresponding absorption has been observed and identified in the gas phase or when a change in chemical bond strengths shifts one of the ion absorptions into a different spectral region that is characteristic of the altered chemical bond. When these criteria are not met, study of the photodestruction characteristics of the ion-containing deposit may be helpful, or the absorption of the neutral which grows in as the ion disappears may provide an important clue. Where several different anion species are present, it is sometimes possible to selectively photodetach one of them. After that anion has been destroyed, on prolonged irradiation the cation concentration will level off at a new, lower value. As is illustrated in Fig. 1, exposure of the deposit to higher energy radiation may result in photodestruction of other, more strongly bound electron traps, resulting in the approach of the
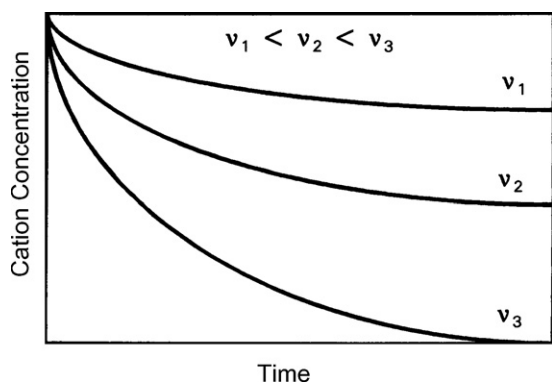

Fig. 1. Cation neutralization resulting from anion photodetachment.

cation concentration to a new, lower asymptotic value. Addition of a supplementary electron donor (e.g., Na, K, Cs) results in enhanced concentration of anions. Alternatively, addition of a supplementary electron captor such as NO_2 or CCl_4 (used as a source of Cl atoms, which serve as the electron captor) may enhance the concentration of cations which are stabilized and/or extend the range of stability of cations on exposure to visible and near ultraviolet radiation. When NO_2 is used, the infrared absorption of NO_2^- grows as less strongly bound anions are photodetached. At higher photon energies, NO_2^- also undergoes photodetachment, and the ion concentration of the sample is depleted.

3.2. Production of anions

Milligan and Jacox [15] demonstrated that charge transfer interaction [16,17] between an alkali metal atom and photochemically generated C_2 leads to the stabilization of C_2^-, the first molecular anion to be observed in a rare-gas matrix. The observed electronic band system of C_2^- had previously been tentatively identified in the gas phase by Herzberg and Lagerqvist [18]. A more complete account of the assignment of this band system of C_2^- has recently been given [19], and the role of charge transfer in anion stabilization in matrix isolation experiments has been reviewed [20].

The demonstration that spontaneous or photoinduced charge transfer interaction of an alkali metal with an electron captor leads to anion stabilization in rare-gas matrices was useful for obtaining infrared spectra of a number of other molecular anions, included in Table 1. However, significant complications arise in some experimental systems. The ν_3 absorption of SO_2^- appeared almost $50\,cm^{-1}$ higher in experiments in which it is formed without introducing an alkali metal into the system [21], supporting a proposal [22] that absorption by $M^+SO_2^-$ contributes to the infrared spectrum when an alkali metal is present. Although CO_3^-, like NO_3^-, is expected to possess D_{3h} symmetry, two prominent CO-stretching absorptions were assigned to CO_3^- in a matrix isolation study [23], requiring that the CO_3^- be distorted to C_{2v} symmetry. Smith et al. [24] reported that the infrared spectra of several metal nitrates trapped in various matrices also showed pairs of absorptions contributed by NO_3 stretching fundamentals. They attributed this splitting to anion distortion by the electrostatic field of the nearby metal cation. A similar explanation may account for the splitting of the CO_3 stretching absorptions of CO_3^-.

3.3. Photoionization

Shortly after the first experiments on the stabilization of anions in rare-gas matrices, infrared absorptions of CCl_3^+ and $HCCl_2^+$ were identified in an argon-matrix study of the 122 nm (10.2 eV) photolysis of chloroform. The cation products resulted from photoionization of the corresponding neutral species formed in the primary photodissociation process; these two free radicals have ionization energies below the 10.2 eV emission of the hydrogen discharge lamp [25]. The CCl-stretching absorptions of both CCl_3^+ and $HCCl_2^+$ appeared at considerably higher

Table 1
Small molecular ions for which infrared spectroscopic data have been obtained using charge transfer, photoionization, and modified discharge sampling

Ion	Matrix	References
BF_2^+	Ne	[92]
BF_3^+	Ne	[92]
BF_3^-	Ne	[92]
BCl_2^+	Ne	[93]
BCl_3^+	Ar	[26]
	Ne	[93]
BCl_3^-	Ne	[93]
$HCCH^+$	Ne	[94]
	Ar	[95]
CN^-	Ne	[96]
HCN^+	Ne	[96]
HNC^+	Ne	[96]
H_2O^+	Ne	[47]
CO^+	Ne	[52]
$OCCO^+$	Ne	[52]
$OCCO^-$	Ne	[52]
CO_2^+	Ne	[40,42]
$(CO_2)_2^+$	Ne	[42,97]
CO_2^-	Ar	[41]
	Ne	[40,42]
$(CO_2)_2^-$	Ne	[42,97]
CO_3^-	Ar	[23]
CO_4^-	Ne	[98]
$HOCO^+$	Ne	[81]
HCO_2^-	Ne	[81,82]
$HCOOH^+$	Ne	[81,82]
OCS^+	Ne	[99]
OCS^-	Ne	[99]
CF_3^+	Ne	[100]
CF_3^-	Ne	[100]
SiF_3^+	Ne	[101]
SiF_3^-	Ne	[101]
$HCCl_2^+$	Ar	[25,34]
CCl_3^+	Ar	[25]
H_2CCH^-	Ne	[10]
$H_2CCCH_2^+$	Ne	[10]
NH_3^+	Ne	[73]
NH_4^+	Ne	[80]
N_4^+	Ne	[53]
NO^+	Ne	[61]
NO_2^+	Ne	[102]
NO_2^-	Ar	[103,104]
	Ne	[102]
N_2O^+	Ne	[105]
NH_2NO^+	Ne	[89]
$ONNO^+$	Ne	[62]
NNO_2^-	Ar	[104]
	Ne	[105]
$(NO)_3^-$	Ne	[62]
NF_2^+	Ne	[106]
NF_2^-	Ne	[106]
NF_3^+	Ne	[106]
PF_2^+	Ne	[107]
PF_3^+	Ne	[107]
PF_3^-	Ne	[107]
PF_4^+	Ne	[107]
PF_4^-	Ne	[107]

Table 1 (*Continued*)

Ion	Matrix	References
PF_5^-	Ne	[107]
F_3PO^-	Ne	[107]
O_3^-	Ar	[55,108]
	Ne	[109]
O_4^+	Ne	[54,59]
O_4^-	Ar	[55]
	Ne	[54]
SO_2^+	Ne	[21]
SO_2^-	Ar	[22,110]
	Ne	[21]
F_2SO^+	Ne	[111]
SF_3^+	Ne	[111]
SF_4^+	Ne	[111]
SF_4^-	Ne	[111]
SF_5^+	Ne	[111]
SF_5^-	Ne	[111]
SF_6^-	Ne	[111]
$HFFH^+$	Ne	[45]
H_2CFH^+	Ne	[112]
HCl^+	Ne	[113]
$HClClH^+$	Ne	[113]
$ClHCl^-$	Ar	[114]
	Ne	[113]
CH_3Cl^+	Ne	[112]
H_2CClH^+	Ne	[112]
HBr^+	Ne	[115]
$HBrBrH^+$	Ne	[115]
$BrHBr^-$	Ar	[116]
	Ne	[115]
CH_3Br^+	Ne	[112]
H_2CBrH^+	Ne	[112]
HI^+	Ne	[115]
$HIIH^+$	Ne	[115]
IHI^-	Ne	[115]
HAr_2^+	Ar	[28–30]
HKr_2^+	Kr	[28–30]
	Ar	[31]
HXe_2^+	Xe	[32]

frequencies than their counterparts for the uncharged species. Similar results were obtained by Miller and Andrews [26] for the degenerate BCl_3 stretching fundamental of $^{11}BCl_3^+$ isolated in solid argon.

For many years, rare-gas containing species of formula HRg_2^+ have been familiar to the mass spectrometrist. In discharge sampling studies of mixtures of H_2 with argon or krypton, infrared absorptions were observed by Bondybey and Pimentel [27], who attributed them to interstitial H atoms trapped in the rare-gas lattice. Subsequently, Milligan and Jacox [28] observed these same infrared absorptions in vacuum ultraviolet photolysis experiments and presented evidence for their contribution by HAr_2^+ and HKr_2^+. This reidentification was later supported and extended by workers in several other laboratories [29–31]. Moreover, Kunttu et al. [32] stabilized HXe_2^+ in a xenon matrix

in concentration sufficient for infrared study upon photoexcitation of a hydrogen halide into a charge transfer state, with consequent charge delocalization.

3.4. Discharge sampling

In the early days of matrix isolation experiments, many different samples were deposited after having been passed through a discharge. Success was limited; atomization of the starting molecule and isotopic "scrambling" in the recombination processes prevailed. A few strongly bound diatomics such as N_2, CO, and CN and some products of their subsequent reaction were detected.

Even under mild discharge conditions, several difficulties attend this type of sampling. The possibility of energy overload and, consequently, poor isolation is always present. Species which possess a large amount of translational energy are likely not to be trapped efficiently on the cryogenic sampling surface. Charge exchange occurs readily in many ion-containing systems. Finally, the rare gas solid provides an energy sink, readily deactivating atoms or molecules whose excited states might be important in the generation of the product of interest.

A modified discharge configuration has been demonstrated to circumvent these problems and has been useful for stabilizing polyatomic ions in many different systems. Jacox [33] first used the discharge sampling configuration shown in Fig. 2 to study dilute mixtures of various small molecules with argon. Pure argon passes through a tube, where it is excited by a microwave discharge before passing through a coarse pinhole (approximately 1 mm in diameter) in the end. The molecule of interest, XY, is introduced downstream from the pinhole as a dilute Ar:XY mixture, which interacts with excited argon atoms and their resonance radiation before being frozen onto the cryogenic observation surface.

When Ar:HCCl$_3$ and Kr:HCCl$_3$ samples were deposited using this modified discharge system, consistently high yields of $HCCl_2^+$ and of anions were obtained [34]. Exposure of the initial deposit of an Ar:HCCl$_3$ sample to ultraviolet irradiation through various cutoff filters demonstrated a threshold for marked growth in the concentration of HAr_2^+, with concomitant photodestruction of $HCCl_2^+$, near 260 nm. Using the proton affinity of CCl_2 determined by Lias and Ausloos [35] and that for argon [36], the calculated threshold for proton transfer from $HCCl_2^+$ to argon was 254 nm. In the argon matrix, cluster formation of the initially formed ArH^+ with a nearest neighbor argon atom ensues. When
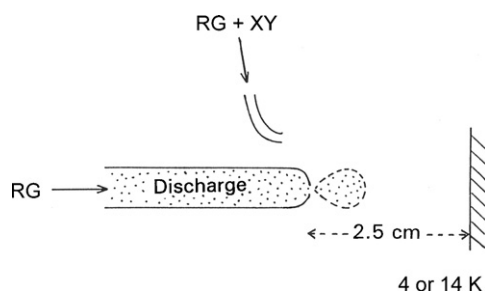

Fig. 2. Modified discharge sampling configuration.

krypton was substituted for argon, the threshold for growth of the HKr_2^+ absorption was both calculated and observed to be somewhat lowered. These results strongly support the earlier HAr_2^+ and HKr_2^+ identifications [28].

The product distributions observed in the argon-matrix experiments using this modified discharge configuration corresponded to those accessible in the 11.5–11.8 eV energy range of the first excited states of argon atoms. Many small molecules have first ionization energies above that range, suggesting that their cations would not be produced using argon atoms as the energy source. Neon, for which the first group of excited energy levels lies between 16.6 and 16.85 eV, appeared to be ideal for photoionizing those molecules. Neon also has the advantages of exceptionally low polarizability and near-zero electron affinity.

Knight [37,38] successfully used excited neon atoms with a variation of the modified discharge sampling configuration to produce small molecular cations with relatively high first ionization energies, such as CO^+, in sufficient concentration for detection by the highly sensitive technique of electron spin resonance.

CO_2 was chosen for a test of the utility of the modified discharge sampling configuration with neon as the rare gas for obtaining infrared spectra of small molecular ions. The first ionization energy of CO_2 is 13.8 eV, requiring the use of excited neon atoms to provide a suitable cation yield. Moreover, the v_3 band center of gas-phase CO_2^+ had been determined [39] to lie at 1423.08 cm^{-1}. In this first study [40], v_3 of CO_2^+ trapped in solid neon appeared at 1421.7 cm^{-1}, only 1.4 cm^{-1} below the gas-phase band center. v_3 of CO_2^-, produced as a result of photoelectron capture by CO_2, appeared at 1658.3 cm^{-1}, appreciably above the range of the bands previously assigned [41] to that fundamental of CO_2^- produced by charge transfer with various alkali metal atoms. A later study [42] led to the identifications of the other infrared-active fundamentals of CO_2^+ and CO_2^- isolated in a neon matrix.

The modified discharge configuration has since been used with neon for many studies of ion spectra. The ions obtained in these experiments are summarized in Table 1. The products are consistent with the generalizations that (a) fragment ions with appearance energies above 16.85 eV are not observed; (b) the parent molecule remains outside the discharge region, so that extensive photofragmentation and isotopic randomization do not occur; and (c) electrons produced on photoionization are captured by other species in the system, yielding an electrically neutral overall deposit.

In the matrix, cage recombination of molecular fragments may suppress net photodestruction of the species of interest. Photodetachment of anions often occurs at a relatively low energy. The observed photodetachment threshold for anions in a neon matrix is usually 1–2 eV higher than the gas-phase photodetachment threshold, because low-energy electrons may more readily recombine with the adjacent molecule than escape from the site of their release. Electrons detached from anions may diffuse through the solid and neutralize cations, reducing their concentration.

The relatively low proton affinity of neon reduces – but does not eliminate – the possibility of proton sharing with the matrix,

which may lead to large matrix shifts. Proton sharing with rare gas atoms and clusters has recently been reviewed by Bieske and Dopfer [43] and has been discussed for neon-matrix experiments by Jacox [7]. The magnitude of the frequency shift which results from proton sharing by the species MH^+ with the rare-gas matrix increases as the proton affinity of M approaches that of the rare-gas atom. The proton affinity evaluation and compilation by Hunter and Lias [44] is very useful for assessing the probable extent of proton sharing for various cations trapped in the solid rare gases. Because the proton affinity of helium is not very much lower than that of neon, some protonated species experience substantial frequency shifts even in helium clusters.

When the cation is surrounded by a matrix of rare gas atoms, frequency shifts which arise from proton sharing are somewhat smaller than those for the cation complex with a single rare gas atom. Nevertheless, they may be substantial. Because the proton affinity of the F atom [44] is exceptionally low, approaching that of neon, both interact strongly with the proton. The resulting HF^+ stretching fundamental is lowered by approximately 700 cm^{-1} from that of HF, and may be assigned to strongly bound $NeHF^+$ [45]. Proton sharing also leads to a large matrix shift for ν_3 of H_2O^+ trapped in an argon matrix. Although the gas-phase band center lies at 3259.04 cm^{-1} [46] and the neon-matrix absorption is at 3219.5 cm^{-1} [47], the argon-matrix absorption lies at 3054.9 cm^{-1} [48].

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

As of mid-2006, 87 vibrational fundamental frequencies of small molecular cations had been measured both in the gas phase and in a neon matrix with experimental uncertainties less than or equal to 1 cm^{-1}. (This count omits a few fundamentals for species such as HF^+ which readily share a proton with neon.) The distribution of the deviations of each neon-matrix value from the corresponding gas-phase band center is shown in Fig. 3. As was found for uncharged reaction intermediates,
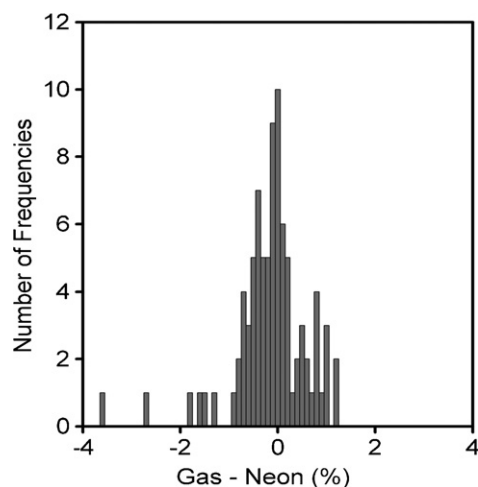
Fig. 3. Comparison of vibrational fundamental frequencies of ground-state cations observed in the gas phase and in a neon matrix.

most cation matrix shifts amount to less than about 1%. Insufficient gas-phase data are available for the corresponding anion comparison.

3.5. Products of ion–molecule reactions

The probability of reaction of many ion–molecule pairs on a single collision is greater than 0.1, two or three orders of magnitude larger than that typical of small uncharged free radicals. These large ion–molecule reaction rates often result in the stabilization of observable concentrations of dimer cations and anions in the modified discharge sampling experiments. Such studies are interesting to both the spectroscopist and the chemist both because of the structural information which can be gained for the complexes and because many of these dimer ions are intermediate in bond strength between van der Waals molecules and typical single bonds.

After their initial discovery of the generation of CO^+ when they used the modified discharge sampling configuration with Ne:CO mixtures, Knight et al. [49] identified several isotopomers of $OCCO^+$ in that system. Their analysis and subsequent theoretical calculations [50] support the *trans*-structure for the cation radical. A later example of the stabilization of an ion–molecule reaction product using this sampling configuration was obtained in the Ne:N_2 experiments of Knight et al. [51], which yielded the electron spin resonance spectrum of N_4^+ isolated in a neon matrix. The accompanying theoretical calculations indicated that N_4^+ is linear. Infrared absorptions of both $OCCO^+$ [52] and N_4^+ [53] were later identified.

Among the early systems studied with the modified discharge configuration was Ne:O_2 [54]. A prominent absorption at 973.1 cm^{-1} was readily assigned to O_4^-, previously identified [55] in argon-matrix experiments in which an alkali metal was the electron source. Although the infrared spectroscopic studies were consistent with the *trans*-O_4^- structure, additional information regarding the positions and isotopic substitution behavior of the low-frequency deformation fundamentals and/or measurement of rotational structure in the gas-phase spectrum would be necessary to distinguish between that isomer and the rectangular one. Later high level ab initio calculations [56] favor the *cyc*-O_4^- structure. Very prominent absorptions appeared at 1164.4 and 1320.3 cm^{-1}, each with isotopic substitution behavior appropriate for an O_4^+ structure which possesses two symmetrically equivalent O_2 moieties, and relatively weak combination bands appeared between 2800 and 3000 cm^{-1}. Concurrent electron spin resonance studies on this system by Knight et al. [57] were consistent with the presence of *trans*-O_4^+ in the system. Although *trans*-O_4^+ possesses only one infrared-active OO-stretching absorption in the mid-infrared, two such absorptions were seen. The assignment problem was resolved by the ab initio calculations of Lindh and Barnes [58], who found symmetry breaking to occur in some ab initio calculations for O_4^+. When an effort was made to circumvent this problem, the calculations suggested that the rectangular and the *trans*-planar isomers of O_4^+ are nearly isoenergetic and are separated by a substantial barrier, suggesting that both forms might have been stabilized in the matrix experiments. Jacox and Thompson [59] showed

that the isotopic substitution data for the O_4^+ absorptions would be consistent with the trapping of both *trans*-O_4^+ and the rectangular isomer in solid neon. In a later study, Zhou et al. [60] found that the 1164.4 cm^{-1} neon-matrix absorption of *trans*-O_4^+ shifted to 1118.6 cm^{-1} in an argon matrix, suggesting that there is significant interaction of *trans*-O_4^+ with the rare gas.

In modified discharge sampling experiments on Ne:NO samples [61,62], a very prominent absorption appeared at 1619.2 cm^{-1}. This absorption behaved similarly to an absorption which appeared at 1593.3 cm^{-1} in Ar:NO experiments using a chemical ionization sampling technique that favored anion stabilization [63]. Accordingly, it was initially assigned to *trans*-ONNO$^-$. A series of gas-phase threshold photoelectron studies [64–66] later showed definitively that this absorption is contributed by the cation, with its gas-phase band center at 1618.2 cm^{-1}.

ONNO$^+$ presents an enormous challenge to the theoretician. Calculations suggest that the *cis*- and *trans*-isomers are nearly isoenergetic. The study by East and Watson [67] favored a planar *cis*-structure. Xie et al. [68] showed that symmetry breaking is important, and somewhat favored a *trans*-ground-state structure. Xie and Schaefer [69] conducted a more detailed analysis of the system using Brueckner methods, and concluded that both the *cis*- and *trans*-isomers should have a prominent infrared absorption near 1600 cm^{-1} but that the *cis*-isomer lies about 0.36 eV above the *trans*-isomer. Later, Xie et al. [70] explored the possibility of a cyclic isomer using density functional theory and high level ab initio methods and concluded that such a structure might contribute the unassigned 1424 cm^{-1} absorption observed in the neon-matrix experiments.

Subsequent laser-ablation studies by Andrews et al. [71] yielded the spectroscopic identification of *cis*- and *trans*-ONNO$^-$ trapped in an argon matrix. Both isomers were later seen in similar neon-matrix experiments [72].

In the modified discharge sampling experiments on Ne:NH$_3$ samples [73], in which NH$_3^+$ was the major product, weak absorptions appeared near the positions of the infrared-active fundamentals of gas-phase NH$_4^+$, $\nu_3 = 3343.14$ cm^{-1} [74–77] and $\nu_4 = 1447.22$ cm^{-1} [78,79]. Hydrogen was added to the sample in an attempt to enhance these absorptions, and various discharge configurations were tried – including passing both molecules through the discharge region – to optimize the yield. The results were compared in Fig. 1 of the resulting paper by Jacox and Thompson [80]. The modified discharge configuration with both H$_2$ and NH$_3$ introduced beyond the discharge region produced the most prominent absorptions of NH$_4^+$. Extensive isotopic substitution was employed, and infrared absorptions were assigned to all of the deuterium-substituted NH$_4^+$ species.

In the study of a Ne:H$_2$:CO$_2$ mixture deposited using the modified discharge sampling procedure [81], many of the product absorptions corresponded to those which had been identified in the companion Ne:HCOOH study [82]. The four vibrational fundamentals which were seen in the infrared spectra were complementary to those obtained, with 20 cm^{-1} uncertainties, in recent gas-phase photoelectron spectroscopic studies [83,84]. Taken together, the photoelectron and infrared studies identified seven of the nine vibrational fundamentals of HCOOH$^+$.

Prominent infrared absorptions of HCO$_2^-$ also appeared in the Ne:HCOOH and Ne:H$_2$:CO$_2$ experiments on formic acid. Subsequently, Krekeler et al. [85] performed high-level ab initio calculations on HCO$_2^-$. Their calculated frequencies and isotopic shifts for that species are in excellent agreement with those observed in the neon-matrix study; all of the frequencies agree with the neon-matrix values within 15 cm^{-1}, and the calculated and observed ^{13}C- and ^{18}O-isotopic shifts agree within 0.7 cm^{-1}. The CH-stretching fundamental of HCO$_2^-$ lies at an exceptionally low frequency, implying a relatively weak CH bond.

An absorption at 3280.9 cm^{-1} was more prominent in the Ne:H$_2$:CO$_2$ experiments than in the Ne:HCOOH experiments. Amano and Tanaka [86,87] had assigned the gas-phase band center for the OH-stretching fundamental (ν_1) of HOCO$^+$ at 3375.37 cm^{-1}. Since HOCO$^+$ was an expected product in both of the discharge sampling systems and since Dopfer et al. [88] had reported that the ν_1 fundamental of gas-phase HOCO$^+$ is lowered by 126.5 cm^{-1} on complexation with a single neon atom, the approximately 95 cm^{-1} disparity between the gas-phase and neon-matrix bands probably results from proton sharing. Two other infrared absorptions, at 2400 and 1020 cm^{-1}, appeared near the calculated positions of HOCO$^+$ fundamentals and had isotopic substitution behavior appropriate for their assignment to the C=O stretching and OH deformation fundamentals, respectively, of HOCO$^+$.

A modified discharge sampling study of the Ne:H$_2$:N$_2$O system – isoelectronic with Ne:H$_2$:CO$_2$ – led to the identification of five of the vibrational fundamentals of NH$_2$NO$^+$ [89]. The attachment of the two H atoms to the end N atom of NNO agrees with the NH$_2$NO$^+$ structure inferred from the neutralization-reionization experiments by Egsgaard et al. [90]. The OH-stretching fundamental of HONN$^+$ was also identified, but was shifted 43.3 cm^{-1} from the gas-phase band center [91] because of proton sharing with the neon matrix.

4. Outlook

Studies of the infrared spectroscopy of molecular ions trapped in rare-gas matrices have much to offer to the ion chemist. These studies have yielded information on the structures and chemical bonding properties of many small molecular ions and ion–molecule complexes, and promise to continue to do so. As quantum chemical theory matures, the experimental results are valuable in refining approximations used to simplify calculations of ion properties. The experimental data also provide information which can be used to aid the in situ search for these intermediates in gas-phase reaction systems. It is hoped that this work will spur the development and improvement of procedures for gas-phase studies.

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