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Frontiers in the spectroscopy of mass-selected molecular ions

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Abstract

Recent developments have made it possible to produce a variety of novel ionic molecular species and to study their spectroscopy. In this article, new ion production schemes and/or modified ion sources for these experiments are discussed, as are various mass spectrometry configurations used for mass selection. New kinds of ions and new forms of sensitive and selective spectroscopy in the ultraviolet, visible, and infrared wavelength regions for these ions are also reviewed. (Int J Mass Spectrom 200 (2000) 545–569) © 2000 Elsevier Science B.V.

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1. Introduction

Since the beginning of mass spectrometry, there has been a fascination with the structures, energetics, and reactivities of positive and negative ions. However, spectroscopic measurements on ions have always been a problem because of the low densities produced and the extreme conditions under which they are formed. Some of the first studies looked at the emission spectra of ions in electrical discharges [1]. In this hot environment, many quantum states are populated and spectra are complex with many broad and overlapping lines. The spectra of some simple ions could be measured in this way, but the ions were sometimes identified incorrectly due to unanticipated impurity species. In a complex environment such as an electrical discharge, many species are in excited electronic states, and emission between different excited states may occur. It is often difficult therefore to connect emission results to absorption measurements in which molecular species originate in the ground electronic state. In many cases, the ions desired for study cannot be produced effectively in discharges or they have low emission yields. For these reasons, more sophisticated techniques have been developed over the years to produce specific ions in high yields, to size select them from mixtures and to measure detailed information about their energy levels. This article focuses on the recent progress in these areas.

Ion spectroscopy remains a very prominent research area because of the advantages that ions provide for hard-to-study molecular systems. It was shown many years ago that photodetachment of negative ions provides access to the ground state of various neutral free radicals [2]. Such radicals are usually found only as transient reaction intermediates and they often cannot be produced in pure form by other methods. Likewise, a popular research area now is the study of atomic and molecular clusters. For

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example, the discovery of C_{60}, which led to various areas of fullerene and carbon nanotube materials research, initially involved mass spectrometry studies of carbon clusters produced in a molecular beam [3]. It is of interest to measure the properties of clusters as a function of the size of the system to see how atomic and molecular characteristics evolve toward bulk solid and liquid phenomena. Ionized clusters which can be mass selected make it possible to study size specific properties in a systematic way. Many fundamental chemical and physical phenomena are intrinsically ionic by nature. For example, the solvation of various ionic compounds necessarily must involve metal cations and their corresponding anions. Ions are used for the production and processing of materials, e.g. semiconductor thin films, and the optimized efficiency of such processes relies on a detailed knowledge of the species present in these plasmas and their concentrations and state distributions. Likewise, ions are present in the atmosphere, in the interstellar medium [4] and in combustion environments. Again, detailed energetic and structural information is required for kinetic models of these systems. In these circumstances and others, it is important to have detailed spectroscopic information for molecular ions.

In many ways, ion spectroscopy is already a mature field of study. For example, the classic series of spectroscopy books by Herzberg, which were all written prior to 1970, contain many examples of small diatomic and polyatomic ion spectra that were detected by discharge emission experiments [1]. Several monographs have been written over the years focusing on ion spectroscopy [5–10]. These earlier volumes describe many classic experiments which provide the foundation for the research ongoing today. The first mass-selected experiment took place in 1962, when Dehmelt and Jefferts measured the spectrum of H_2^+ in a quadrupole ion trap [11]. Other notable early developments include the application of microwave absorption spectroscopy to ions in discharges by Woods and co-workers, which provided high resolution measurements for many small ions [12]. Oka measured the infrared absorption spectrum of H_3^+ in discharges, likewise providing high quality structural data [13]. To make infrared spectroscopy more general, Saykally and co-workers developed velocity modulation techniques for discharges which allowed ion spectra to be distinguished from more intense signals from neutral species [14]. Likewise, Saykally and co-workers provided the first measurements of infrared absorption spectroscopy for mass-selected ion beams [15]. The group of Y.T. Lee provided some of the first infrared photodissociation measurements on mass selected ion beams [16], while Mosely and co-workers [17] and Carrington and co-workers [18] provided similar early measurements in the visible and ultraviolet regions. Lineberger focused on the photoelectron spectroscopy of negative ions [19] and obtained high resolution spectra with laser autodetachment spectroscopy [20]. The techniques pioneered in these and other groups are still in use today, and variations on these themes constitute many of the new developments in ion spectroscopy in the present age.

This article examines recent progress in ion spectroscopy with an emphasis on the particular techniques and classes of ions which form the focus of present research efforts. The article is organized around the three key areas essential for ion spectroscopy: ion preparation, mass-selection, and optical detection. The first requirement is the preparation of desired ions in high densities distributed over a few initial quantum states, so that the measurement scheme will have enough sensitivity and so that the spectral information will be of high quality. Almost all ion production schemes yield a mixture of ions, and mass selection is essential for an exact identification. However, mass selection must preserve ion density and the method employed must carry the ions in a convenient way to the spectroscopy measurement. Even before mass selection, ion densities are low, and so the spectroscopy employed must be sensitive. Some schemes use measurements which have inherent high sensitivity (i.e. some form of laser spectroscopy), while others store ions in various ways to integrate density or to increase the interaction time with the light source. The focus here is on optical spectroscopy techniques, which provide higher resolution spectroscopy, and the article therefore does not cover the full breadth of work done in areas such as photoelectron spectroscopy. Of course all of these areas of consideration have benefited from new technology including new kinds of mass spectrometers, more convenient computer control and interfacing, as well as new laser light sources. We will consider here some of the recent developments in each of these areas which are providing exciting new data for ion spectroscopy.

2. Ion sources

Ions are conventionally formed in mass spectrometers with electron impact or chemical ionization [21–23]. Other methods may include Penning ionization, electrical or microwave discharges [21–23]. However, these familiar processes are usually inconvenient for ion spectroscopy because they make hot ions. For best ionization efficiency, these processes usually work at energies well above the ionization threshold, and considerable excess energy is deposited into the internal degrees of freedom of the molecular ions produced. This excess energy causes the familiar fragmentation patterns which form the basis of structural analysis in mass spectrometry. Even in so-called "gentle ionization" schemes (e.g. chemical ionization), a broad distribution of internal states are produced, which give rise to broad and overlapping bands in vibrational or electronic spectra. These various ionization processes are well-studied in mass spectrometry, and it is understood that the Franck-Condon factors connecting the neutral with its corresponding cation determine the states populated [24]. These processes rarely result in the production of ground state ions. Similar arguments can be made for electron attachment to neutrals to form negative ions.

Improvements can be made if ions are prepared at higher pressure in a buffer gas so that collisional energy transfer can relax the excited electronic and vibrational states. This strategy is used in the well known "flowing afterglow" method, where ions in a fast flowing gas mixture at pressures near 1–10 Torr are generally regarded to be thermalized to the flow tube temperature [25]. Room temperature is often cool enough to obtain spectra for smaller ions, and many studies are described in the literature. For example, flowing afterglow sources have been incorporated into photoelectron spectroscopy measurements by Lineberger and co-workers [26]. Leone and co-workers have used laser induced fluorescence spectroscopy of ions in flow tubes and drift tubes to study collisional energy transfer and reaction dynamics [27]. However, the ions available for study with flowing afterglows are those that come from gas phase precursors via conventional ionization methods. If more exotic ions are desired or if additional cooling is required, further improvements are necessary.

Various forms of electrical discharges have been used to produce and study ions for over 150 years [28,29]. Hollow-cathode or glow-discharge sources incorporated into flowing afterglows have provided spectra of many ionic species. Metal-containing ions and metal atom cluster ions have also been produced with these methods [30,31]. For metal ion experiments, a flowing buffer gas such as argon is ionized by a cylindrically symmetric discharge between a central wire and an outer tube composed of the metal of interest. Sputtering of the tube electrode around the inner wall by rare gas cations yields gas phase metal. This is a common way to produce atomic metal cations for studies of their reactivity. Larger clusters of metal atoms may also be produced by this method. For example, Lineberger and co-workers have studied the photoelectron spectroscopy of Cu_x^- and Ag_x^- species [30]. The advantage of this source is that ions are essentially thermalized and there is a continuous ion beam. However, the instantaneous density of metal clusters produced is much less than in pulsed laser vaporization sources (see the following), and laser sources make it possible to grow much larger clusters. Additionally, hollow cathode sputtering sources require that the material which is sputtered be a conductor, and so these sources are not appropriate for many materials.

Closely related to hollow cathode discharge sources are the so-called corona discharge sources. In the corona discharge, there is also a cylindrical electrode with a central wire, but the exit end of the electrode is enclosed to provide a higher pressure in the discharge region. There is a small diameter exit hole in the closed end which provides a mild supersonic expansion as the gas exits into a flow tube or molecular beam. In this way, the ions produced are colder than those from other discharge sources. Saykally and co-workers used this configuration in their early studies of ion infrared spectroscopy [15].

To obtain better cooling and to form ionic molecular clusters, electron impact ionization may be combined with a pulsed supersonic expansion. This kind of source has been used by many research groups to produce negative ions and their clusters, e.g. $I_2^-(H_2O)_n$, $Br_2^-(CO_2)_n$, for studies of photodissociation spectroscopy, photoelectron spectroscopy, and even time resolved recombination and caging reactions. Photoelectron spectroscopy measurements using this source have been described by Lineberger and co-workers [19,20,31,32], Johnson and co-workers [33], Bowen and co-workers [34,35], Neumark and co-workers [36–42], etc. Photodissociation spectroscopy measurements have been described by Lineberger and co-workers [43–45], Johnson and co-workers [46–53], Lisy and co-workers [54,55], Okumura and co-workers [56,57] and others. Positive ion clusters, e.g. Ar_n^+, may also be produced [32]. In this method, a pulsed nozzle provides an expansion of a pure atomic or molecular gas or a molecular species seeded in rare gas. A metal wire filament or indirectly heated cathode is situated 1–2 cm downstream from the expansion. A draw-out grid provides an electron beam with kilovolt energies which crosses the expansion. This electron gun produces ions directly via electron impact or by charge transfer or Penning ionization reactions between the rare gas and the molecular species. Clusters which have already grown in the supersonic expansion may become ionized and cool partially via evaporation of rare gas or molecular units. There is some modest amount of additional cluster growth and/or collisional cooling downstream of the excitation, but at this point the gas density is falling rapidly. The advantage of this kind of source is that it is inexpensive to build and operate, and that it produces a variety of ions. However, it has recently been recognized that this source has disadvantages for spectroscopy. Although ions are produced in a supersonic expansion, they are not effectively cooled in this configuration. Apparently, cluster growth and cooling are nearly complete prior to the point where ionization occurs, and the energy deposited in the ionization process causes evaporative cooling of the ions to a level determined by the binding energy of the ions and the timescale of the detection. The net result is that there may be considerable complexity found in spectra of such ions due to their incomplete cooling. For example, Johnson and co-workers have recently studied the infrared photodissociation spectroscopy of $I_2^-(H_2O)_n$ clusters and $I_2^-(H_2O)_xAr_y$ clusters produced by this source [52,53]. The argon-tagged clusters are presumed to be much colder than those clusters not having argon attached because of the much weaker binding energy. The argon-tagged clusters have sharper and more clearly resolved vibrational structure than those without argon. Questions have been raised about how the argon may perturb the spectroscopy. However, the vibrational structure measured is independent of the number of argon atoms attached, implying that any perturbation is a minor effect. Variations on the jet-electron impact source have been described such as the slit-jet-electron impact source developed by Maier and co-workers [57]. This source allows multipass direct infrared absorption spectroscopy experiments on ions.

Laser photoionization provides an efficient source of ions whose spatial position can be carefully controlled. Ions can be produced via multiphoton excitation with, for example, excimer laser excitation at the F_2 (157 nm; 7.89 eV), ArF (193 nm; 6.42 eV), or KrF (248 nm; 5.00 eV) wavelengths. One photon excitation at these energies is not usually enough for ionization except for certain radical or metal cluster species, but vacuum ultraviolet is absorbed efficiently by many molecules and two-photon ionization is relative efficient with these lasers. Resonance-enhanced photoionization via known neutral molecular excited states may also be accomplished with dye lasers or optical OPO systems. In nonspecific ionization schemes, the Franck-Condon factors for ionization determine the internal state distribution. However, with careful resonant excitation schemes, the final cation species may be produced in specific quantum states. The advantage of laser ionization is that it provides control of the spatial position where ions are produced. For example, ions can be created in the throat of a supersonic expansion for subsequent cooling, or they can be produced within the confines of an ion trap. Recent experiments have used resonance enhanced multiphoton ionization (REMPI) to produce polycyclic aromatic hydrocarbon (PAH) ions or PAH–rare gas complexes for studies of infrared predissociation spectroscopy [58–61].

Laser vaporization in a pulsed nozzle cluster source [62] was initially demonstrated for the production of neutral clusters of metal atoms. However, in more recent work this method has been demonstrated as a general source for the production of cold cations or anions containing metals or other refractory elements (e.g. semiconductors and carbon). In the early work, Smalley and co-workers produced metal dimer and trimer cations and demonstrated photodissociation spectroscopy [63]. Later experiments made larger anions for photoelectron spectroscopy as a function of cluster size for metals [64–66], carbon clusters [67], and semiconductor clusters [68,69]. Subsequent studies in other groups have used diatomic and triatomic metal cations produced this way to measure the onset for photodissociation channels [70–72]. Several other groups have adopted laser vaporization to produce negative ion metal clusters for studies of photoelectron spectroscopy [73–76]. In cluster ions containing multiple metal atoms, vibrationally resolved spectra are rarely obtained because of the high density of electronic states and their complex couplings. However, photoelectron spectra have been useful to measure the progressive onset of electronic energy bands in these spectra as the number of metal atoms increases toward the bulk.

Higher quality spectroscopy with vibrational and even rotational resolution can be obtained for smaller metal-containing molecular ion complexes. In the work of Farrar and co-workers [77–80], Brucat and co-workers [81–90], Fuke and co-workers [91–93], Kleiber and co-workers [94–99], Miller and co-workers [100], Velegrakis and co-workers [101–105], and in the work of our group [106–115], metal cation complexes with rare gas atoms or small molecules have been produced and studied with mass-selected photodissociation spectroscopy or laser induced fluorescence. More recently, neutral metal complexes have been produced by this method for studies of zero electron kinetic energy (ZEKE) or mass analyzed threshold ionization (MATI) photoelectron spectroscopy [116–131]. Laser vaporization is the most efficient pulsed source for ions containing metals. When used properly, it can produce high peak densities of a variety of species cooled to low internal temperatures. Vibrationally and rotationally resolved electronic spectra have been obtained for variety of mass-selected ions. As described below, the pulsed nature of this method makes it especially suited to be combined with time-of-flight mass spectrometer methods. A critical element of laser sources is that the expansion gas must be confined to flow in a channel over the metal sample to maintain the density for metal–metal recombination reactions. Supersonic expansion at or beyond the laser impact point can then lead to efficient supersonic cooling of the ions formed. Designs in which samples are mounted in vacuum downstream from a free jet expansion do not produce cold ions. Likewise, so-called pick-up designs in which other gases are entrained in the beam after the main expansion also do not produce cold ions. These configurations suffer from the same inherent problems as electron impact excitation on jets described above. If ions are produced downstream after the main expansion the cooling, if any, is inefficient.

Modified forms of electrical discharge sources have recently been described by several labs to form molecular ions with efficient pulsed supersonic expansion cooling [132–136]. Molecular ions and molecular ion clusters are produced efficiently by these sources. Carbon cluster ions [137] and silicon cluster ions [138] have been produced via discharge reactions of volatile precursors. Designs have been described which sputter the electrode material to make metal containing ions [133]. The advantage of such a source for these latter experiments is that it is far less expensive than a laser source. However, experience in our lab finds that such sources do not produce as much ion density as laser sources and the ions produced are not as cold. In many discharge sources, the voltage may be applied to the electrodes with a dc power supply and the gas pulse flowing through the interaction region ignites the discharge. However, we and others have found that much better cooling is obtained when the high voltage is pulsed rapidly (a few microseconds) during the middle of the gas pulse. In this way, ions formed by the discharge can be cooled effectively as gas before and after the discharge zone fill in and provide more collisions. In an optimized design, the electrodes should not interrupt the gas flow through the nozzle. Ring electrodes around the circumference of the gas channel provide the best design for this purpose [132,134,135]. In recent experiments, Nesbitt and co-workers have adapted a slit jet discharge for infrared absorption measurements of small molecular ions [136]. Like the Maier source described previously, a multipass arrangement allows IR absorption experiments to be done on ions.

Ion sources that use the methods described previously produce primarily singly charged cations or anions. This occurs because small ions in low pressure gas phase environments usually cannot support multiple charges without spontaneously decomposing to two or more singly charged fragments. Some newer ions sources are successful in extracting ions directly from solution, where solvation stabilizes higher charge states. Electrospray sources are rapidly becoming the most popular source for the study of such multiply charged species [139–143]. Kebarle and co-workers have studied the thermochemistry of multiply charged metal cations from such a source [144], while Posey and co-workers have measured photodissociation spectra of ions produced this way [145–150]. Wang and co-workers have studied multiply charged anions from such a source [151–161] with photoelectron spectroscopy. Stace and co-workers have described a closely related “pick-up” source in which molecular beam expansions pick up metal, solvate it, and then become ionized, thus stabilizing higher charge states and producing multiply charged metal cation complexes [162–166].

3. Mass selection and trapping

Ions have been mass selected for spectroscopy measurements with almost every kind of mass spectrometer conceivable. Many of the traditional methods using sector instruments, quadrupole instruments, etc., have been described in earlier books and review articles. More recent work in ion spectroscopy focuses on mass spectrometer configurations which can be adapted for use with pulsed ion sources, on instruments which store ions to achieve greater interaction times with the light sources or on isolation techniques to integrate ion density. We mention here three general areas which have attracted recent attention: time-of-flight mass spectrometers, ion traps and rare gas matrix isolation experiments.

As described earlier, many of the new ion source configurations take advantage of pulsed gas expansions for increased cooling of internal degrees of freedom. The inherent pulsed nature of these experiments naturally suggests that mass analysis should also be done in a pulsed mode of operation, which logically leads to time-of-flight (TOF) mass spectrometers. TOF instruments have pulsed mass analysis, efficient throughput of ions, and favorable spatial characteristics for overlapping ions with lasers. The ions which traverse such an instrument encounter only high transmission grids, and otherwise they pass through an empty field-free region for mass analysis. 95% or more of the ions which enter the instrument may be detected and analyzed. In the mass analysis process, care is taken to spatially bunch the ions having the same mass. A narrow time-of-flight distribution is necessary for proper mass analysis, and this is an ideal situation for overlapping the ions with laser light. The region in space where ions are most tightly bunched is known as the spatial focus, and this may be adjusted with the ratio of the acceleration fields used. TOF instruments have therefore become increasingly popular for spectroscopy studies involving ion photodissociation and anion photoelectron spectroscopy.

Lineberger and co-workers were among the first to employ time-of-flight mass spectrometers for mass-selected photodissociation experiments [32,167,168].

They used a reflectron TOF instrument, and crossed the ion beam in the linear field-free flight region prior to the reflectron field at the spatial focus of the ion beam. The flight time to this point provides the mass selection of the parent ion of interest. After laser excitation, parent ions and their photofragments, if any, would still have the same velocity and therefore the same flight time to a detector located somewhere downstream. Separation of these different masses requires deceleration and reacceleration so that the ions with different masses have different velocities and therefore different flight times to the detector. This takes place in the reflectron field, and a detector located beyond this reflector can then distinguish fragment ions from their parents with high resolution. The disadvantage of the Lineberger design is that ions are excited in the field-free drift region when they are at high velocities. Timing for excitation with pulsed lasers is therefore somewhat difficult. Additionally, when ions fragment before entering the reflectron region, different mass fragments with the same velocity (derived from the parent) have different energies, and they turn at different positions and follow different trajectories through the reflectron. It may not be possible, therefore, to focus all masses simultaneously on the detector with good efficiency. Bloomfield and co-workers described a simple TOF scheme for photodissociation experiments in which two linear flight tube sections are connected end-to-end with a deceleration/reacceleration region in the middle where laser excitation occurs [169]. This device has easier timing because the ions are moving slowly when excited, and all ions follow essentially the same path to the detector. However, the end-to-end configuration is somewhat awkward because it takes up significant amounts of lab space. Our group has described another reflectron TOF scheme for photodissociation experiments in which the ions are excited in the turning region of the reflectron field [170]. This device has convenient timing because ions are excited at their slowest point in the turning region, and all parent and fragment ions follow essentially the same path to the detector. The reflectron used for this experiment mounts vertically in the lab frame and therefore does not occupy excess space. Each of these configurations of TOF instruments are presently in operation in several labs, as are other designs with variations on these. Most of these instruments now use pulsed deflection plates in addition to the time-of-flight to select parent ions. TOF instruments with a single linear section are also used in several groups to size select anions for photoelectron spectroscopy measurements [33–42].

Another recurring theme in ion spectroscopy is the trapping of ions in Penning- or Paul-type ion traps [171] where optical excitation is possible over an extended time period. While small molecular ions either fluoresce or photodissociate promptly on the microsecond timescale, larger ions undergo radiationless processes more efficiently and energy is converted internally to the ground electronic state. Unimolecular dissociation in such systems may be quite slow or it may require substantial excess energy obtained via continuous excitation (e.g. with a cw laser) or multiple pulse excitation (with a pulsed laser). The optical excitation usually occurs while the ions are trapped, and then they are extracted out of the trap into quadrupole or time-of-flight mass spectrometers for mass analysis. Mikami and co-workers have described a configuration in which a pulsed supersonic beam source ionized via REMPI techniques is injected into an ion trap for subsequent laser excitation [172–177]. Likewise, Meijer and co-workers have studied the vibrational spectra of PAH cations produced via excimer laser ionization and studied with resonance-enhanced infrared laser multiphoton photodissociation with a free-electron laser [178]. In the case of large ionized particles in the micron size domain, ion traps may be used for light scattering measurements to determine extremely high molecular weights [179].

Closely related to ion traps are Fourier transform mass spectrometers. The extremely high mass resolution of these instruments is well recognized, and ion trapping times of several minutes are now commonplace. However, it is relatively difficult to interface these instruments with external ion sources which provide ion cooling, and it is recognized that blackbody emission from the trapping cell walls can reheat ions trapped for long periods. Access to the trapped ions is limited by the position of the cell in the superconducting magnet. Consequently, there have been examples of spectroscopy for ions trapped in Fourier transform instruments [180], but this method has seen only limited applications.

A final interesting aspect of recent ion spectroscopy has been the mass selection of ions followed by deposition and isolation in cryogenic rare gas matrices. Ions have been produced for many years in situ in matrix isolation experiments, but without mass resolution. These kinds of experiments are still actively pursued [181–183]. However, when unusual ions are produced, such as a distribution of clusters, it is essential to have size identification to avoid mis-assigning spectra. Unfortunately, the deposition of a mass-selected beam into a cryogenic matrix presents technical difficulties. Energetic ion beams may melt matrices, or charging of the matrix may occur which deflects further deposition. The deposition rate is also an issue, because ion beams have low density even when integrated over several hours. These issues have been tackled by several research groups, and it is now possible in certain circumstances to size select ion beams and deposit positive or negative ion species. Maier and co-workers have been particularly successful in this endeavor, and have reported the spectroscopy of various linear carbon chain species and partially hydrogenated carbon chain species of astrophysical interest [184–187].

4. Highlights of recent experiments

Since the early days of ion spectroscopy, many small ions from ordinary gaseous precursor molecules have been produced and studied. These systems do not require any special preparation conditions and their study often does not require any special spectroscopic techniques. Emission spectroscopy or IR absorption methods often work for these species. In recent years, however, the focus has been on more exotic ions, and more creative techniques are required for their preparation and study. Atomic and molecular clusters, metal-containing ions, larger molecular ions and multiply charged ions are of increasing interest. In the sections which follow, some of the new experiments in these areas are discussed.

4.1. Small molecular ions

Ions with a limited number of atoms can be studied with vibrationally and rotationally resolved high resolution spectroscopy, and through the rotationally resolved spectra the geometric structures of these ions can be determined. High resolution spectroscopy like this has been a mainstay of ion spectroscopy studies over the years, and it is through such studies that we have obtained much of the structural information that we know about molecular ions. In recent work, these experiments have been extended to small ionic clusters. As pulsed ion sources with increased collisional cooling have been developed, these cluster ions are naturally produced with greater efficiency. However, weakly bound systems are more sensitive to radiationless processes and predissociation, and so the main technique used for these studies has been mass-selected photodissociation spectroscopy.

Maier and co-workers were among the first to study photodissociation spectroscopy of small cation complexes, and they have remained one of the most active groups in this area [188–196]. A recent review article provides a comprehensive overview of the diversity of small cations and anions studied at high resolution [188]. Recent representative examples include NH_4^+–Ar_n [189,190], NH_2^+–He_n [191], HCO^+–Ar_n [192], and N_4^+ [195]. In early work, electronic spectroscopy studies were most prominent because of the increased sensitivity of this method and because of the availability of pulsed dye lasers in the visible and ultraviolet wavelength regions. More recent studies have extended the work to the mid-infrared wavelength regions, especially in the 3.0 μm region where N–H and O–H stretch vibrations have strong activity.

IR studies only became possible with the recent advent of high intensity tunable infrared laser systems. Initially, these studies were limited to the 3.0 μm wavelength range where dye laser difference frequency generation (usually in a lithium niobate crystal) provided some useful intensity (0.1–1.0 mJ/pulse) of IR. More recently, optical parametric oscil-

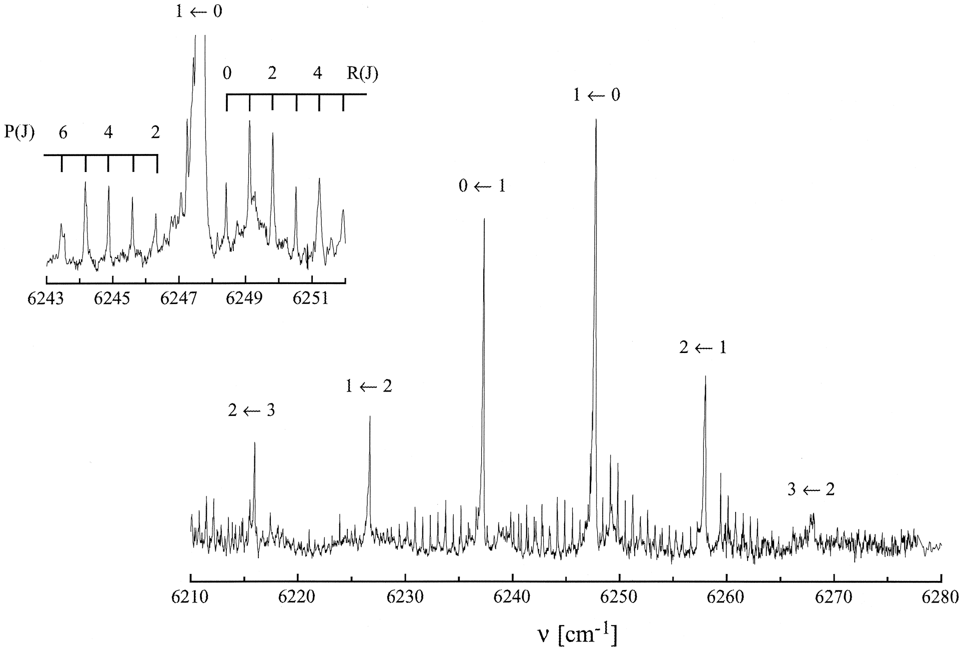

Fig. 1. A high resolution spectrum of the complex CH_3^+–Ar measured with mass-selected infrared laser photodissociation spectroscopy. The spectrum shown is for the overtone region near 6250 cm^{-1}, with the $K'_a \leftarrow K''_a$ *Q* branches labeled. The inset shows the 1 ← 0 subband in more detail along with *P* and *R* branch assignments. Used with permission from [199].

lation (OPO) techniques have provided light in this same wavelength region with higher intensity and extended the available wavelength range significantly. It is now possible, for example, to obtain tunable IR light from OPOs in the 2.0–5.0 μm range with energies in the range of several millijoules/pulse (e.g. 10–15 mJ/pulse at 3.0 μm; 1.0 mJ at 5.0 μm). The availability of good laser sources in the mid-IR region has in fact stimulated many new experiments with neutral clusters [197,198] and with ions.

Figure 1 shows a representative example of these kinds of experiments in the form of a high resolution spectrum of the complex CH_3^+–Ar measured by Dopfer and co-workers with mass-selected infrared laser photodissociation spectroscopy [199]. The ions were formed by electron impact on a jet expansion, mass selected with a quadrupole mass spectrometer, interacted with the laser in an octopole ion guide, and fragments were mass analyzed by a second quadrupole instrument. Spectra were measured in the ν_3 asymmetric hydrogen stretching region and also in the region of the first overtone of the C–H stretch. The spectrum shown here is for the overtone region near 6250 cm^{-1}. As indicated, the spectrum is rotationally resolved with the $K'_a \leftarrow K''_a$ Q branches labeled. The inset shows the 1 ← 0 subband in more detail along with P and R branch assignments. This spectrum indicates that the complex has a pyramidal C_{3v} structure with the argon attached to the empty $2p_z$ orbital on the CH_3^+ moiety.

Negative ion complexes have also been studied with IR photodissociation spectroscopy making use of the same difference-frequency generation and OPO technology developments. Anion complexes are usually much more weakly bound than cations, and one-photon IR photoexcitation in the 3000–3700 cm^{-1} region can lead to efficient elimination of ligand molecules. Okumura and co-workers [56,57], Johnson and co-workers [46–53], and Lisy and co-workers [54,55] have studied the vibrational spectra of $X^-(H_2O)_n$ complexes to investigate the inner solvation shells in these species. Depending on the strength

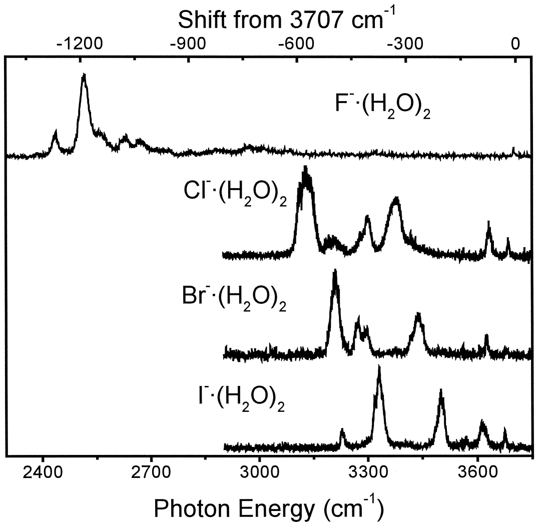

Fig. 2. IR photodissociation spectra measured for various $X^-(H_2O)_2$ complexes in the region of the O–H stretching vibrations.

of the charge–dipole interaction compared to the dipole–dipole interaction of the water molecules, the ion may be "solvated" in the interior of the complex or it may occupy a "surface" position. These issues depend in a sensitive way on the electronegativity of the halogen, which causes the negative charge to be more or less localized. This issue is demonstrated nicely in Fig. 2, where the IR spectra measured by Johnson and co-workers for various $X^-(H_2O)_2$ complexes are presented [47]. In the fluorine complex, the high electronegativity causes more charge localization, and the charge–dipole interaction is strong. Theory and equilibrium mass spectrometry experiments show that the dissociation energy of the 1:1 complex is greater than expected previously (D_0 = 26.4 kcal/mol) and that the $F^- \cdots HOH$ potential is affected by the presence of a "shoulder" minimum structure corresponding to the $FH \cdots OH^-$ species [200]. Consistent with this strong interaction, there is no vibrational activity for the 1:2 complex in the 3000–3400 cm^{-1} region associated with hydrogen-bonded OH. In the higher halogens, however, the charge is more delocalized, and hydrogen bonding is competitive with the charge–dipole interaction. Hydrogen bonded OH is clearly evident in the vibrational spectra. These phenomena were only clearly evident when cooler ions from argon-tagging experiments were studied.

Although photoexcitation of most anions in the visible wavelength region leads to photodetachment, certain anions are strongly bound and can have bound electronic excited states. This is known for various C_n^- and C_nH^- species. In these cases, electronic spectroscopy studies are possible by way of 1 + 1 resonance enhanced photodetachment spectroscopy. Mass-selected anions are excited and depletion of the parent ion signal provides a spectrum. This method has been employed by Maier for studies of C_3^- [184], by Neumark for studies of C_5^- and C_6^- [201], and by Maier for studies of small $C_{2n}H^-$ species [185].

Another recent development in light sources is the Advanced Light Source (ALS), which provides synchrotron radiation in the 6–30 eV energy range with extremely high resolution and convenient tunability [202]. This source also enables new forms of ion spectroscopy. Light in this energy range makes it possible to photoionize a number of small molecules in a direct one-photon process. In the past, high resolution ZEKE photoelectron experiments were limited to aromatic molecular species whose low ionization potentials made it possible to achieve threshold ionization with visible and near-UV lasers in various 1 + 1 REMPI schemes. However, the resolution and tunability of the ALS makes it possible to scan in the threshold region and to carry out high resolution ZEKE photoelectron spectroscopy measurements [203] on species such as NO [204], CO_2 [205], CH_4 [206], C_2H_2 [207], O_2 [208], CO [209], etc. These ZEKE measurements then provide unprecedented detail for the spectroscopy of the corresponding ground state cations. This method has been applied to a number of small molecules thus far, but it has the potential to explore the ground state of numerous molecular cations.

As alluded to above, ZEKE high resolution photoelectron spectroscopy has become a popular method with which to study aromatic molecules which have relatively low ionization potentials (typically 7–9 eV) [210,211]. These systems generally have excited electronic states in the 3.5–4.5 eV range, and it is therefore possible to ionize these species efficiently with 1 + 1 ionization using two independently tunable lasers (dyes or optical OPOs). The result of the ZEKE experiment is vibrational and sometimes rotational information for the ground state of the molecular cation produced. The mechanism of ZEKE and its applications have been reviewed extensively [210,211]. Via various REMPI excitation schemes, high lying Rydberg states ($n \geq 100$) near the ionization threshold are eventually excited, and these states become stabilized toward emission via n–l mixing. After a short time delay of a few microseconds, the application of a pulse electric field can "field ionize" these states, thus giving rise to the alternate name of "pulsed field ionization" (PFI) spectroscopy. In the ZEKE experiment, the electron yield as a function of threshold ionization wavelength is measured, while in the MATI experiment [212] the corresponding positive ions are measured. In the MATI experiment, an advantage is that there is mass analysis of the species being ionized, but a small dc electric field must be applied to separate ions formed directly by the lasers from those near-threshold ions produced via PFI. Rydberg series are present in essentially all molecules, and there are different series converging to the initial ionization threshold (i.e. the $v = 0$ level of the cation) as well as to higher vibronic thresholds corresponding to a vibrationally excited cation core. Therefore, these methods provide an excellent probe of the ground state cation vibronic structure. In favorable circumstances, rotationally resolved spectra can be obtained.

ZEKE and MATI experiments have now been pursued for several years on stable molecular species and on van der Waals complexes of these species. New variations of these methods attracting current interest are applications to unstable molecular species (e.g. the metal-containing systems indicated below) and the application of the new PIRI technique (photoinduced Rydberg ionization spectroscopy) [213–215]. In the PIRI method, pulsed laser excitation is employed to ionize the highly excited Rydberg states rather than a pulsed electric field. In the early versions of the method, the laser was a visible dye laser tuned to cation excited electronic states [213–215]. When the cation core-plus-high Rydberg electron system is excited this way, autoionization occurs out of the cation core excited state, and both a positive ion and an electron are produced. However, in this method no electric fields need to be present to separate directly formed ions, and so higher resolution may be obtained than in typical MATI experiments. In more recent versions of PIRI, new infrared laser technology (OPOs) have been applied to vibrationally excite the cation core and ionization takes place by means of autoionization of these levels [216]. This provides cation vibrational spectra with normal IR selection rules.

Another variation on the ZEKE theme is the new technique developed by Hepburn and co-workers known as threshold ion-pair production spectroscopy [217–219]. It can be shown that there are Rydberg-like states converging to energetic thresholds in which a neutral molecule separates into a cation/anion pair, and a form of threshold PFI spectroscopy can be conducted on these states (e.g. $HCl \rightarrow H^+ + Cl^-$). These thresholds usually occur at high energy, and tunable vacuum UV sources have been used thus far to probe these systems. From the thresholds obtained for triatomic species, diatomic ionic ground state structure can be obtained and neutral thermochemistry can be determined with high precision.

Cavity ringdown spectroscopy has become a fashionable spectroscopy technique for some applications because it has relatively high sensitivity and because it is a direct absorption spectroscopy technique [220,221]. Consequently, the detection scheme does not rely on emission, dissociation, etc., which might occur after absorption. Although cavity ringdown is far more sensitive than conventional absorption spectroscopy, its sensitivity is not as great as mass spectrometry-based methods. Molecular ions have been studied with cavity ringdown [222], but this method has not been exploited significantly thus far for ion spectroscopy.

4.2. Larger molecular ions

As molecular ions increase in size they are more difficult to produce in the gas phase in high density and they have spectroscopy with increased complexity. Intramolecular radiationless processes become more rapid in larger systems and both emission and photodissociation processes become increasingly inefficient in these systems. High temperatures are often required to achieve significant vapor pressures of large species. For these various reasons, the spectroscopy of large molecular ions has been somewhat limited.

Maier and co-workers have overcome some of these problems for large carbon chains and partially hydrogenated carbon chains by making the ions in a discharge or electron impact source and then depositing them in a cryogenic rare gas matrix [184–187,223,224]. Deposition of large molecules is not as severe a problem as it is for small molecules because of their inherent stability and slow dissociation rates. By deposition in a matrix, the concentration can be sufficiently increased to obtain enough material for study. With greater density, direct UV–VIS and IR absorption methods can be used to overcome the difficulties with emission or photodissociation yields. Spectra of several carbon cation and anion systems have been obtained [184–187,223,224] for comparison to the optical diffuse interstellar bands (DIBS) [225]. A representative series of spectra is shown in Fig. 3 for the overlapping (1) $^2\Pi \leftarrow X\ ^2\Pi$ and (2) $^2\Pi \leftarrow X\ ^2\Pi$ electronic transitions of $HC_{2n}H^-$ species ($n = 6$–12), which were isolated in neon [186]. As shown, there is a systematic redshift in the origin band positions with the length of the carbon chain. Resonance enhanced photodetachment spectroscopy has also been applied in the gas phase to some of these linear carbon chain species [185,226]. In the case of C_7^- [226] seven sharp bands are measured in the optical region. Five of these match exactly with the positions of known DIBS, and the two other lines are obscured by broad DIBS. C_7^- is thus the best match so far for laboratory spectra with DIBS. However, it is not clear why this particular carbon chain species would be more abundant than others in the interstellar medium.

Slow dissociation rates in large organic ions can be overcome by rare gas tagging experiments like those mentioned earlier for small ions. A number of groups have used photodissociation of PAH^+–rare gas complexes, for example, to study the optical and IR spectra of these species [58–61].

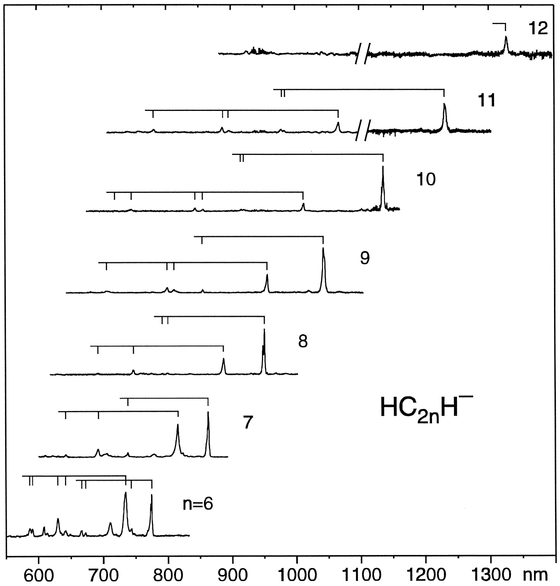

Fig. 3. Series of spectra for the overlapping (1) $^2\Pi \leftarrow X\ ^2\Pi$ and (2) $^2\Pi \leftarrow X\ ^2\Pi$ electronic transitions of $HC_{2n}H^-$ species ($n = 6$–12), which were mass selected and matrix isolated in neon. Used with permission from [186].

Meijer and co-workers have demonstrated another novel approach to overcome slow unimolecular dissociation rates in their study of cations of polycyclic aromatic hydrocarbons [178]. Neutral vapor from an oven source is introduced into an ion trap where it is ionized by pulsed excimer laser excitation. The cations produced are trapped and excited repeatedly with a pulsed free electron laser in the 400–1700 cm^{-1} region. By such excitation, the ions are able to absorb many photons and become hot enough internally so that photodissociation eventually occurs. Fig. 4 shows such a spectrum for the cation of pyrene. The inset shows the mass spectrum measured by extraction of the ions from the trap into a time-of-flight spectrometer. The parent ion is offscale and the small peak indicated with an arrow is the C_2H_n mass loss channel. Measurement of this channel while the free electron laser is scanned provides a resonance enhanced photodissociation spectrum in the IR region. Like other developments indicated above, this exper-

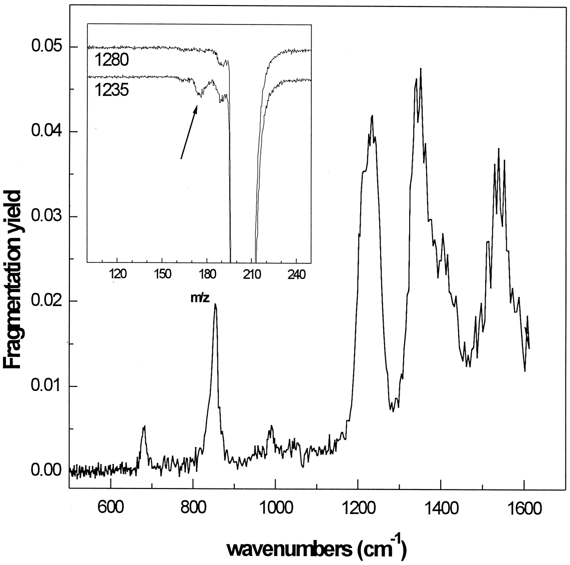

Fig. 4. Infrared photodissociation spectrum for pyrene cation obtained by trapping the ions in a Paul trap and exciting them repeatedly with the FELIX free electron laser. The inset shows the mass spectrum measured by extraction of the ions from the trap into a time-of-flight spectrometer. The small peak indicated with an arrow is the C_2H_n mass loss channel. Measurement of this channel while the free electron laser is scanned provides the spectrum.

iment is only possible with the availability of a new light source, the free electron laser for infrared experiments (FELIX), which is able to provide high peak powers of broadly tunable light in the mid- and far-IR regions.

PAH species have also been the subject of large molecular anion studies. Weinkauf and co-workers have used threshold photodetachment methods to determine the electron affinities for various PAH species [227]. PAH anions and their clusters can be produced from oven sources or from laser ablation methods for study with photoelectron spectroscopy [228]. Kaya and co-workers (including this author) studied the electron affinities of coronene (EA = 0.47 eV) and its clusters and found a steady increase in EA as cluster size increases [228]. Weinkauf and co-workers have also used the threshold detachment method to study so-called "dipole-bound" anions of large molecular species such as nucleic acid bases (e.g., uracil, thymine, cytosine) and their clusters with water [229]. Dipole-bound anions have negligible covalent electron affinity, but are able to bind an external electron to the dipole moment of the system. Photoelectron spectroscopy has been the technique of choice to study these systems, and these experiments are continuing. More recently, small molecular clusters have been a research focus of this work (e.g. water clusters [230]), as have dipole-bound anions of the nucleic acid bases (e.g. uracil) [231].

In the limit of extremely large ions, Wang and co-workers have produced a variety of multiply charged anions with an electrospray ionization source and studied them with photoelectron spectroscopy [151–161]. They show that dynamic stability plays a significant role in the stability of large multiply charged anions. The electronic potential can be thought of as a long-range coulomb repulsion superimposed with a short-range electron binding component. As a consequence, a repulsive coulomb barrier (RCB) can occur in the detachment coordinate. It was shown for dicarboxylate dianions, $O_2C(CH_2)_nCO_2^-$ [160] and citric acid [158] that photoexcitation energies well above the photodetachment threshold do not lead to detachment. Likewise, in the case of the cyclic copper phthalocyanine (CuPc) moiety, the addition of multiple sulfonate groups ($-SO_3^-$) forms complexes such as $[CuPc(SO_3)_4]^{4-}$. These species have multiple negative charges, but the bound portion of the potential lies behind a RCB at an energy as much as 0.9 eV above that of the complex asymptotic species. In this sense, these complexes exhibit a negative electron binding energy [161].

4.3. Metal-containing ions

Since the development of laser ablation sources, pulsed discharge sources and electrospray sources, many of the new advances in ion spectroscopy have included metal-containing ions. The early work in molecular beams using laser ablation made pure metal cluster ions, e.g. M_n^+ or M_n^-. Photodissociation was employed for cation species [63] and photoelectron spectroscopy was employed for anion species [64–66,73–76]. However, few spectra of metal cluster ions were obtained with sharp structure which could be analyzed. The problems of high electronic state density and complex electronic/vibronic couplings and predissociation apparently preclude vibrationally resolved electronic spectra in the same way that these effects limit the spectra which can be obtained for neutral metal clusters. Vibrational spectroscopy for metal clusters is expected to occur at low frequencies in the far infrared, and the unavailability of light sources here has precluded such studies. There has been recent progress in this area for neutral metal clusters and metal compound clusters (e.g. carbides) using "infrared resonance enhanced multiphoton ionization" (IR-REMPI) with a tunable free electron laser [232,233], but these methods have not yet been applied for ions. ZEKE spectroscopy has been applied to small metal clusters and their compounds [116–127], but not to clusters with more than four metal atoms. The present status therefore is that there are few vibrationally resolved spectroscopic studies for multimetal atom cluster ions, and there are no viable methods with which to directly measure structures.

The prospects are much improved, however, for ions containing only a single metal atom in a complex with rare gas atoms or small molecules. These metal ion complexes are prototypes for metal–ligand interactions and for studies of nascent metal ion solvation. With only a single metal present, the density of excited electronic states is much lower and electronic spectroscopy can isolate discrete transitions with assignable vibronic structure. Fluorescence [100], photodissociation [77–115,234–239] and photoelectron spectroscopy [120,128–131,240] techniques have been used to probe these complexes and this area has flourished in the last few years.

For most metal complexes, when an ion interacts with a closed-shelled atom or molecule, insertion chemistry is unlikely and the complex is best described as a metal atom interacting with a ligand. For relatively unreactive metals, such as the lighter alkalis and alkaline earth elements or the group III metals, it is usually expected that the interaction between the metal and the ligand will have a strong electrostatic component, and these complexes may be viewed as ion–molecule complexes. This is true because the ionization potential of these metal atoms lie in the range of 6–8 eV, while small molecular species and rare gas atoms have ionization potentials that are much higher. With these energetics, the charge in the system is highly localized on the metal, and the system can be viewed as $M^+–L_n$, where the binding involves the charged atom interacting with the various electrostatic moments of the ligand species. Ab initio theory of these systems confirm that this is an accurate picture of the bonding [241–253], and the spectroscopic measurements made are in excellent agreement with theory on this point. Additionally, collision-induced dissociation measurements of bond energies for these complexes are also consistent with electrostatic bonding [254]. A similar situation applies for transition metal ions in complexes with rare gas atoms. However, transition metal complexes with various molecular ligands have been shown to have more covalent character in their bonding [255].

In the complexes bound primarily by electrostatic forces, qualitative structures and binding energies can be easily predicted. More importantly, electronic spectra can also be predicted. If the interaction between the metal cation and the ligand is indeed weak, then the atomic resonances on the isolated metal cation should be found in these complexes with small shifts in energy and multiplet splittings coming from the details of the interaction. This concept is indeed valid, and it has been exploited by various groups to probe the excited states of these systems via electronic spectroscopy. The electronic states of rare gas atoms and/or closed-shelled small molecules lie at much higher energies, and so ligand-based electronic transitions are not usually seen. Likewise, ionization potentials of the isolated metal atoms can be used to estimate the ionization potentials of complexes, and this has been exploited for ZEKE and MATI photoelectron spectroscopy studies of neutral complexes, which probe the ground electronic state of metal cations.

The group II metal cations have been a focus area for studies of metal cation complex electronic spectroscopy because of the strongly allowed $^2P \leftarrow {}^2S$ atomic resonance which these metals possess. With one valence electron in an ns orbital, the electronic structure of these systems is particularly simple; they are isoelectronic to the neutral alkali atoms. The ground state of cation complexes are derived from the ns^1 (^2S) + ligand asymptote, and excited states are derived from the np^1 (^2P) + ligand asymptote. In Mg^+, these are the only states at low energy, while in heavier metals (Ca^+, Sr^+, Ba^+) there are also excited molecular states derived from the $(n - 1)\ d^9\ ns^2$ (^2D) + ligand asymptote. Although the $^2D \leftarrow {}^2S$ atomic transition is forbidden, transitions between some of the molecular states derived from this transition are allowed and have been shown to have good intensity.

In some of the earliest work in this area, Farrar and co-workers used photodissociation spectroscopy to study various complexes of water and ammonia with Sr^+ [77–80] near the $^2P \leftarrow {}^2S$ atomic resonance in Sr^+. As in other subsequent studies, excitation of the mass-selected parent ion was accomplished with a tunable dye laser which populated the bound excited state, and then dissociation occurred via either absorption of another photon or predissociation of the bound state. It is of course difficult to determine the exact dissociation mechanism in these experiments. When dissociation occurred, the fragment ion(s) intensity was measured as a function of wavelength to obtain an action spectrum. Structure in these spectra were assigned to specific electronic states and there was some vibrational structure resolved. Fuke and co-workers studied Mg^+ and Ca^+ complexes with multiple water molecules and noted the occurrence of excited state photoinduced reactions which produced metal hydroxide masses [91–93]. After a critical size of five water molecules, hydroxide product ions were observed directly in the source distribution, indicating a spontaneous solvation reaction. In later work of this same type, our group has performed extensive studies of Mg^+ complexes and Ca^+ complexes with the rare gases (Ne, Ar, Kr, Xe) [107,111,113] and with various small molecules (H_2O [106,114], N_2 [109], CO_2 [112], C_2H_2 [110], CH_3OH [115], etc.). In these latter experiments, the ion source produces much colder ions and extensive vibrational structure and rotational structure is resolved for a number of monoligand complexes. However, multi-ligand complexes are found to undergo photoinduced reactions and/or rapid predissociation, and no sharp vibrational structure was found. The only exception to this is the recently studied complex Ca^+–Ar_2, which is concluded from the spectroscopy to be linear [256]. Kleiber and co-workers have also reported a number of vibrationally resolved spectra for Mg^+ and Ca^+ complexes (CH_4, C_2H_4, CH_3OH, etc.) [94–99], and Velegrakis and co-workers have focused on rare gas complexes with Sr^+ [101–105]. In closely related work, Brucat and co-workers have measured vibrationally and rotationally resolved spectra for transition metal (V^+, Co^+, Ni^+) ions with numerous rare gases and small molecules [81–90].

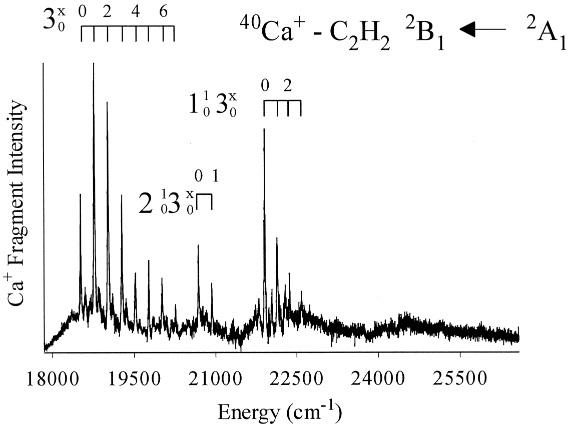

Fig. 5. Photodissociation spectrum of Ca^+–C_2H_2. The parent ion was produced by laser vaporization in a pulsed nozzle expansion, mass selected in a reflectron time-of-flight, and photodissociated near the Ca^+ ($^2P \leftarrow {}^2S$) atomic transition.

A representative spectrum of the Ca^+–acetylene complex is shown in Fig. 5 [110]. The interesting question in this system is whether the calcium ion binds to the side of the C≡C bond in the so-called π-complex configuration, or whether it forms a metal–vinylidene Ca^+–CCH_2 complex. Both are predicted to lie close in energy by theory. The π complex would involve weak electrostatic interactions (charge-quadrupole binding), while the vinylidene complex would have more covalent interactions. The spectrum is located near the Ca^+ ($^2P \leftarrow {}^2S$) atomic transition, consistent with the electrostatic bonding. The vibrational progression at low energy has a frequency in the excited state of $\omega_e' = 258\ cm^{-1}$, which is also consistent with the frequencies measured previously

Table 1
The spectroscopic properties of Mg^+–L complexes measured with electronic photodissociation spectroscopy; the first excited state energies are redshifted from the Mg^+ ($^2P_{1/2,3/2} \leftarrow {}^2S$) transition at 35 699/35 761 cm^{-1}; the redshift is greater for more strongly bound complexes

Complex	Origin (cm^{-1})	ω_e' (cm^{-1})	D_0'' (kcal/mol)
Mg^+–Ne	34 086	219	0.27
Mg^+–Ar	31 456	272	3.70
Mg^+–Kr	30 464	258	5.50
Mg^+–Xe	28 825	258	12.0
Mg^+–CO_2	29 625	382	14.7
Mg^+–H_2O	28 396	517	25.0

for other weakly bound metal cation complexes. This progression is assigned to the Ca^+–C_2H_2 stretching mode. As noted above, activity in this mode is expected because of the different metal–ligand interactions in the excited electronic state compared to the ground state. Additionally, other higher frequencies are observed with intervals near 2170 and 3400 cm^{-1}, consistent with the known C–C stretch and symmetric hydrogen stretch in acetylene. These bands shift in the way expected when the Ca^+–C_2D_2 complex spectrum is measured. The Ca^+–C_2D_2 complex spectrum also shows activity in the cis-bending mode. These various frequencies are almost the same as they are in isolated acetylene, again indicating a weak electrostatic bonding. Rotationally resolved spectra determine the rotational constants expected for the π complex and the even:odd line alternation expected for equivalent hydrogens. All of these combined observations confirm that the complex giving rise to this spectrum is indeed the π complex with side-on metal ion binding. This is the first example of spectroscopy which is able to confirm the structure of an isolated π-complex.

The concepts learned through these various studies can be illustrated by consideration of the trends in a series of complexes with the prototype cation Mg^+. The energetics and spectroscopic constants measured for selected complexes are shown in Table 1. In each complex studied, an electronic spectrum with sharp vibrational structure was found near the atomic transition in Mg^+, but it is shifted in energy to the red from this wavelength. In diatomic (metal–rare gas) and linear polyatomic (metal–CO_2 –N_2) complexes, the sharp spectrum was associated with the $^2\Pi_{1/2,3/2} \leftarrow X\ {}^2\Sigma^+$ electronic transition. In nonlinear complexes (metal–water, metal–acetylene), the states were those expected for the appropriate symmetry (e.g. C_{2v}) correlating to the ^2P metal excited asymptote. The red shift in energy for these electronic spectra can be understood via the differential binding energies for the complexes in their excited versus ground electronic states. For example, the ground state of Mg^+–rare gas species is $^2\Sigma^+$, which corresponds to a metal cation with one electron in a rather diffuse 3*s* orbital. The interaction of this electron with a close-shelled rare gas involves both charge-induced dipole forces and significant electron–electron repulsive forces in the valence shell. Consequently, the ground state binding is expected to be rather weak. In the excited $^2\Pi$ state, however, the valence electron is in a 3*p* orbital oriented perpendicular to the molecular axis. In this configuration, the attractive forces are enhanced because the doubly positive ion core is exposed to the ligand, and the repulsive forces are essentially eliminated because the electron density is off axis. The excited state binding is thus much greater than the ground state binding, and the differential effect causes the spectrum to be red-shifted. This same effect is found for all the group II cations in these states, and similar orbital alignment effects are found in excited states for the heavier metals at the M^+ (^2D) + ligand excited asymptote.

The binding energies in the complex excited electronic state can be determined by extrapolating the extended progressions measured in the metal–ligand stretch vibration. This mode has the greatest Franck-Condon activity due to the change in the metal–ligand bonding interaction. Extrapolation procedures (e.g. Birge-Sponer versus Le Roy-Bernstein methods) for these progressions have been discussed in detail [108]. When excited state dissociation energies are determined from an extrapolation, the ground state dissociation energy can also be determined from an energetic cycle using the origin band position and the atomic transition energy, $D_0'' = \nu_{00} + D_0' - E\,(^2P\text{–}{}^2S)$. The bond energies in Table 1 were derived in this way. As expected, the Mg^+–rare gas complexes are more weakly bound than metal–molecular complexes because of the weak charge-induced dipole interaction. The lighter rare gases are more weakly bound due to their lower polarizability. The Mg^+–CO_2 complexes has an intermediate bond energy because of the dominant charge-quadrupole interaction, whereas the Mg^+–H_2O complex has the strongest interaction of those shown here due to the strong charge-dipole interaction. In cases where data is available, the metal–ligand bond distances can be rationalized in a similar way.

As noted above, transition metal complexes have been studied in great detail by Brucat and co-workers [81–90]. However, in these systems there is already a greater density of electronic states and it is not always possible to determine which atomic states give rise to the molecular states under study. There are no electronic spectroscopy studies of complexes with the alkali metal cations because these species have no excited states at low energy. Likewise, main group metals other than those in group II have not been studied extensively because their excited states also occur at high energy. Dagdigian has made some recent progress in this area using vacuum UV generation techniques to study the electronic spectroscopy of aluminum ion complexes [234].

Although alkali cation complexes cannot be studied easily with electronic spectroscopy, Lisy and co-workers have been successful in studying these species with infrared photodissociation spectroscopy [235–239]. In this method, new infrared OPOs are employed which provide light in the 3.0 μm wavelength region. This makes it possible to excite the ligand-based vibrations which occur in this wavelength region. These include the O–H stretches of species such as water or methanol and the C–H stretches of various organic small molecules. Metal–ligand stretching or bending modes are expected at much lower frequencies and are not usually accessible in these experiments. Using the same logic discussed above, if the binding interactions are weak, the ligand vibrations will have essentially the same frequencies that they do in the isolated free molecules. The potential problem with these experiments is that the excitation energy at the one-photon level near 3000–3700 cm^{-1} is less than the expected bond energies of the complexes, e.g. M^+–H_2O complexes are expected to be bound by 20–25 kcal/mol, which is 7000–8700 cm^{-1}. Therefore, one-photon excitation of these vibrations cannot dissociate the complexes. Lisy's approach has been to use complexes which are not produced in their ground state, i.e. they are already somewhat hot internally from the ionization process (electron impact). The IR excitation therefore adds to this existing internal energy, providing enough total energy to obtain a convenient dissociation rate. The spectra exhibit some rotational profile broadening, but they are sharp enough to identify the essential elements of the vibrational spectrum. For example, free O–H stretches are known to occur near 3650 and 3750 cm^{-1}, while hydrogen bonded O–H vibrations (donor or acceptor) occur at lower frequencies near 3000–3200 cm^{-1}. Thus, these IR spectra reveal which complex sizes have the "solvent" molecules attached to the metal and which have second-sphere hydrogen-bonded ligands. Likewise, in the case of mixed-ligands, these IR spectra can reveal which is preferentially attached to the metal. In this latter vein, mixed complexes of Na^+ and K^+ were studied with water and benzene ligands. Fig. 6 shows selected spectra for $K^+(benzene)_mH_2O$ complexes [235]. The Na^+ preferentially binds water, whereas for K^+ the binding

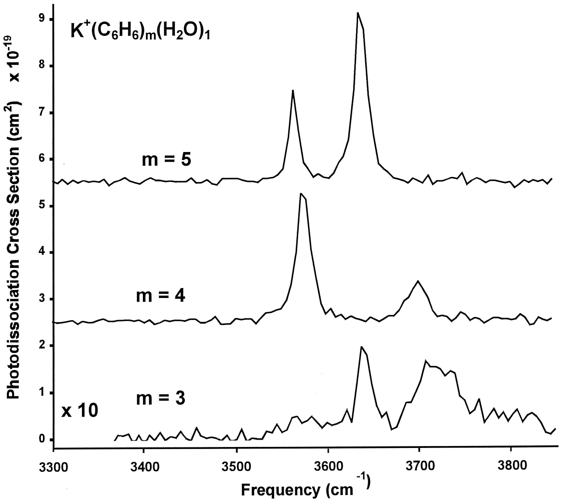

Fig. 6. Infrared photodissociation spectra of several $K^+(benzene)H_2O$ complexes in the C–H and O–H stretching region.

with benzene is competitive with that for water. These trends are argued to explain the different selectivity for these two metals in ion transport through cell membranes [235].

ZEKE and MATI spectroscopies provide another way to probe the ground state vibrational spectra of metal cation complexes. If these experiments are done on covalently bound metal complexes, then careful searching is required to locate the ionization potential. Miller and co-workers [128,129] have studied several covalently bonded complexes. However, if these experiments begin with neutral metal van der Waals complexes, the ionization potential (IP) of the complex is usually close to, but lower than, the IP of the isolated metal atom. In either case, complexes are ionized at threshold to produce the corresponding ground state cations. Although IR photodissociation spectroscopy probes the IR-active vibrations in the higher frequency range, these experiments favor symmetric vibrations, especially those which involve the metal–ligand stretch coordinate. Low frequency vibrations which would occur in the far-IR region in the IR spectrum can be measured without difficulty in these spectra. While electronic spectroscopy requires metal cation resonance lines at convenient energies, these experiments require metals with low ionization potentials. Therefore, alkali metals and the group III main group metals (Al, In, Ba) have been the focus of these studies.

Weakly bound metal complexes have been the focus of many ZEKE and MATI studies because the ground state cations formed exhibit the same kinds of electrostatic interactions expected for metal ion solvation. Alkali metal complexes with water and ammonia have been studied by Blake and co-workers [240], while both our group [120,131] and that of Yang [130] have examined the group III metals. We have studied MATI spectra of Al^+–Ar [120] and ZEKE spectra of Al^+–H_2O and Al^+–D_2O [130], whereas Yang has studied Al^+ and In^+ in complexes with NH_3.

Fig. 7 shows the ZEKE spectra measured by Yang for the (a) Al–NH_3 and (b) In–NH_3 complexes. The total energy of ionization in both cases is lower than the respective metal ionization potentials. This results from the differential binding energy of the neutral (with a van der Waals interaction) and the cation (with a charge–dipole interaction). The Al–NH_3 complex exhibits a progression in a frequency of 339 cm^{-1} which is assigned to the metal–ligand stretch, and there is a satellite progression spaced 58 cm^{-1} away from each member due to the aluminum spin–orbit splitting. The progression labeled (c) arises from the $v = 1$ hotband level in the metal–ligand stretch (222 cm^{-1}) in the ground state. As is sometimes found in these spectra, the ZEKE measurement also determines the fundamental for the neutral complex. The In–NH_3 complex exhibits a similar progression in the metal–ligand stretch with a frequency of 234 cm^{-1}. These spectra measure only the lower vibrational frequencies, but they probe a significant portion of the metal–ligand potential. They complement IR photodissociation measurements which probe only the higher frequency ligand modes.

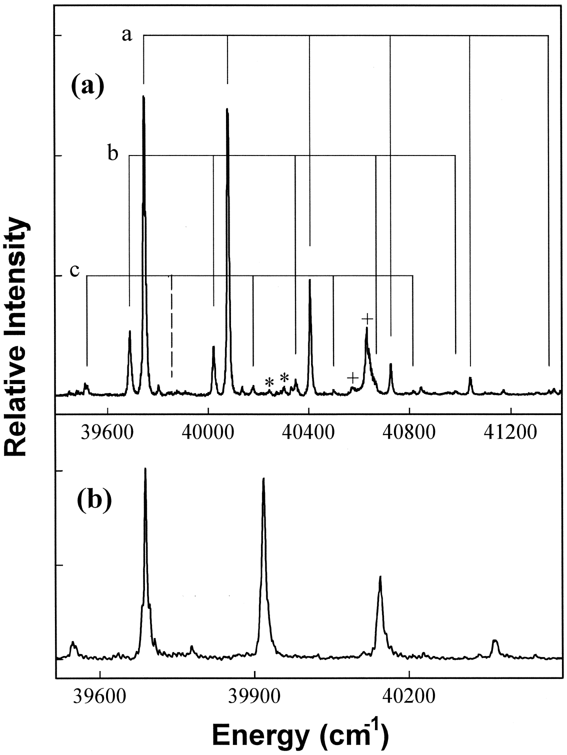

Fig. 7. ZEKE spectra of (a) Al–NH_3 and (b) In–NH_3 showing strong progressions in the metal cation–ligand stretch in the respective ground electronic states.

The various measurements described here for electronic and vibrational photodissociation and for ZEKE and MATI photoionization have produced much information on the electronic states, vibrational frequencies and dissociation energies of metal cation complexes. In almost every system, electrostatic bonding is believed to dominate the interactions. Theory has examined these same systems and provided much guidance throughout these studies [241–253], and the interaction between experiments and theory has been fruitful. Likewise, spectroscopic measurements on metal cation complexes have been complemented by collision induced dissociation measurements and other thermochemical measurements on these same systems [254]. Anion complexes of metals with small molecules have been produced in preliminary experiments in our lab, e.g. $Ag^-(H_2O)_n$, but these systems have not yet been studied in detail.

In complexes with metal ions attached to larger molecular ligands, it is rare to obtain vibrationally resolved spectroscopy. However, other interesting electronic and geometric structural issues arise. Metal ion–benzene complexes provide interesting electronic effects because the ionization potential of benzene (9.24 eV) is almost as low as the IPs of metal atoms. Complexes have been studied with silver (IP = 7.58 eV), magnesium (IP = 7.65 eV), iron (IP = 7.87 eV), etc. [257,258]. In each of these cases, the charge in the complex is expected to be localized on the metal because of the IP difference. However, optical excitation in the visible and near-UV region can exceed the IP difference between the metal and ligand, and charge–transfer electronic states can be excited. When the excitation energy exceeds the IP difference and the ground state bond energy, efficient formation of the benzene cation occurs via photodissociation. For example, the silver ion is closed-shell and has no low energy atomic states. The benzene neutral has its first excited π–π^* transition near 260 nm. However, the Ag^+–benzene complex absorbs strongly in the blue visible wavelength region via a charge transfer resonance. Because the ionization potential differences are known, the threshold for the appearance of the charge–transfer channel, where the energy must be large enough to break the bond and transfer the charge, can be used to establish the bond energies in these complexes.

Complexes of benzene with the early transition metals give rise to remarkable mass spectra with magic numbers at the stoichiometries $[M_n(\text{benzene})_{n+1}]$. Kaya and co-workers [259,260] have proposed that these stoichiometries represent multiple-decker sandwich structures. These features are especially prominent for vanadium, but they are also seen for other early transition metals. Bowers and co-workers have confirmed these proposed structures by way of ion mobility measurements [261]. Photoelectron spectra have been measured for the metal–benzene anion complexes, but there is no detailed spectroscopy experiment which can measure these structures. Similar mass spectral patterns have been seen for the ions of lanthanide metals with cyclooctatetraene [262]. Closely related to this work are various studies of metal complexes with C_{60} (exohedral) [265–267] and with polycyclic aromatic hydrocarbons [268–270,228]. In both cases, interesting questions arise about where metal attachment occurs on the surface of the aromatic system (bridged or ring-centered sites). Likewise, Martin has demonstrated the formation of multiple metal clustering around the C_{60} core, with mass abundances suggesting the growth of complete surface films and multiple layers of metal [263–265]. Kaya has studied complexes richer in C_{60} and found stoichiometries suggesting multiple decker sandwiches [266,267] and other networks. Photoelectron spectroscopy has been measured for some of these complexes, but again there is no detailed spectroscopy to confirm structures. Dunbar has produced complexes with metal cations and polycyclic aromatic hydrocarbons via reactions of metal ions with PAH vapor [268]. Our research group has produced metal and multiple metal complexes with polycyclic PAH species [269,270,228] using laser vaporization of a metal sample coated with a thin film of the organic. We find mass distributions and photodissociation patterns consistent with the addition of multiple metal atoms on the same side of the aromatic and with sandwich structures. Photoelectron spectroscopy of V–(coro-

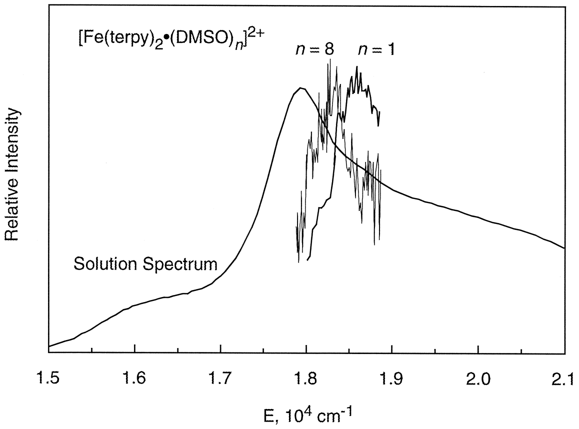

Fig. 8. Photodissociation spectra of $[Fe(terpy)_2]^{2+}$ $(DMSO)_{1,8}$ ions produced by way of electrospray from a solution of dimethyl sulfoxide (DMSO). The spectra in the metal-to-ligand charge transfer region are compared to the absorption spectrum of the solution. Used with permission from [149].

nene)$_2^-$ complexes find evidence for sandwich and non-sandwich isomers [271].

One of the most fascinating new developments in metal ion complexes has been the ability to produce multiply charged metal cation complexes directly from solution with electrospray ionization [145–150] or other methods [162–166]. The metal complexes produced by this methods are more representative of the normal species present in solution, and thus these studies are able to probe solvation dynamics. However, multiply charged metal cations do not have low energy excited electronic states, and so metal-based transitions are not available. However, charge-transfer type resonances are prominent in these species, just as they are in solution. A representative spectrum obtained by Posey and co-workers is shown in Fig. 8. In this figure, cations of bis(2,2′:6′,2″-terpyridyl)iron (II), i.e. $[Fe(terpy)_2]^{2+}$ are produced via electrospray from a solution of dimethyl sulfoxide (DMSO). Photodissociation action spectra in the region of the metal-to-ligand charge transfer band for complexes with one or eight solvent molecules are compared to the same complex in DMSO solution [149]. Photoexcitation in this region leads to evaporation of solvent, which is detected with the mass spectrometer. The spectrum shows a measurable shift with the number of solvent molecules present. These and other spectra for up to 11 solvent molecules show that about 60% of the bulk solvent reorganization energy is obtained even in these small systems. Stace and co-workers have studied a similar charge-transfer photodissociation mechanism in [Cu(pyridine)$_n$]$^{2+}$ and [Ag(pyridine)$_n$]$^{2+}$ produced using their beam-gas pick-up source [166].

5. Conclusions

The various work described here represents a selection of the recent progress in mass-selected ion spectroscopy. New ion sources and new mass-selection techniques are described as are many new spectroscopic methods. As is usual in such areas, technological developments have made much of the progress possible. Some of the most recent developments include new ways to make novel large ions and new ways to make multiply charged ions. The spectroscopy of these species is in its infancy, but progress is expected as these methods are adopted in other labs. Likewise, much progress has been possible via new laser sources. Vacuum UV technology has been around for several years, but this is still only adopted in a few labs. However, perhaps the most exciting laser developments have been in the infrared region. Free electron lasers have provided a hint of the measurements possible in the far-IR, and OPO sources are rapidly becoming routinely available in the mid-IR. Continued progress in spectroscopy of molecular ions is expected as these sources are employed more broadly and as they are extended to longer wavelengths. Thus, although ion spectroscopy already covers extensive areas of chemistry, we can expect continued expansion of this field in the future.

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