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APPLICATIONS OF FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY IN COORDINATION CHEMISTRY

PAUL SHARPE and DAVID E. RICHARDSON

Department of Chemistry, University of Florida, Gainesville, FL 32611 (U.S.A.)

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CONTENTS

ABBREVIATIONS

acac	acetylacetonato
aIP	adiabatic ionization potential
CI	chemical ionization
bpy	2,2′-bipyridine
EA	electron affinity
FAB/MS	fast-atom bombardment mass spectrometry
FD	field desorption
FTICR/MS	Fourier transform ion cyclotron resonance mass spectrometry
hfac	hexafluoroacetylacetonato
ICR/MS	ion cyclotron resonance mass spectrometry (drift cell)
m/z	mass-to-charge ratio

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A. INTRODUCTION

The chemistry of metal compounds in the gas phase has received increasing attention in the last several years. Although some of the work is concerned with non-ionic species [1–4], much of the published research considers ion molecule processes involving metal-containing ions (mostly derived from organometallic precursors) or bare metal ions (produced via techniques such as laser vaporization of pure metals) [5–16]. The elegant work of many groups in the area loosely described as gas-phase organometallic chemistry has been reviewed [17,18] and will not be included here. The great bulk of this latter work has centered on the reactions of bare metal ions or highly coordinatively unsaturated metal ions with C–H and C–C bonds. Relatively little attention has been given to coordinatively saturated metal complexes with non-carbon donor ligands. In this review, we will describe the applications of the powerful FTICR/MS technique [19–22] in the study of gas-phase reactions and properties of metal complexes with primarily non-carbon donor ligands. In particular, the focus will be on the study of gas-phase kinetics and thermodynamics of ion–molecule processes rather than on analytical mass spectrometry for identification of unknowns [23].

In Sections B and C we will describe the theory of operation of the instrument and various sampling techniques relevant to compounds with low volatility. The theory of ion cyclotron resonance and FTICR/MS has been reviewed extensively elsewhere [24,25], and the reader is referred to those articles for in-depth descriptions. Here we will only provide sufficient detail to allow an appreciation of the descriptions of applications to coordination compounds given in Section D. As the use of FTICR/MS and other methods for studying ion–molecule reactions of coordination compounds is only now developing, some possible future directions for research are described throughout the text.

B. DESCRIPTION OF THE FTICR/MS TECHNIQUE

(i) Production, trapping and mass analysis of ions

The FTICR/MS technique is based on the classical motion of ions described by elementary laws of electromagnetism. The magnetic force (Lorentz force, $F = q(V \times B)$) acting on a particle of mass M, charge q, and initial velocity V in a field of magnetic induction B causes it to follow a helical path (Fig. 1). The constrained circular motion has a frequency in hertz given by $\nu_c = qB/2\pi M$. This frequency is the cyclotron frequency and falls in the range of radiowave frequencies (0.01–2.00 MHz) for magnetic

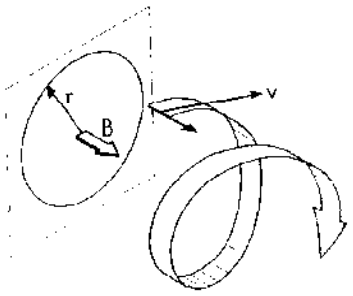


Fig. 1. Ions with initial velocity V are constrained to a helical path along the axis of the magnetic field.

fields of the order of 1 T. To prevent ions from travelling along the helical path and being lost, ions are produced between two trapping plates perpendicular to the magnetic field. These plates are maintained at a repulsive potential (typically + 1 V or - 1 V for positive and negative ions respectively), and the ions thereby are held in a defined region between the two plates.

Excitation and detection of the trapped ions require two additional sets of plates (transmit and receive plates) lying along the axis of the magnetic field between the trapping plates, so that the heart of the FTICR/MS is a box-shaped cell of six plates. Cells are typically cubic [26] with each plate of area ca. 1 in^2 (Fig. 2). The cell is mounted in a high vacuum chamber in a

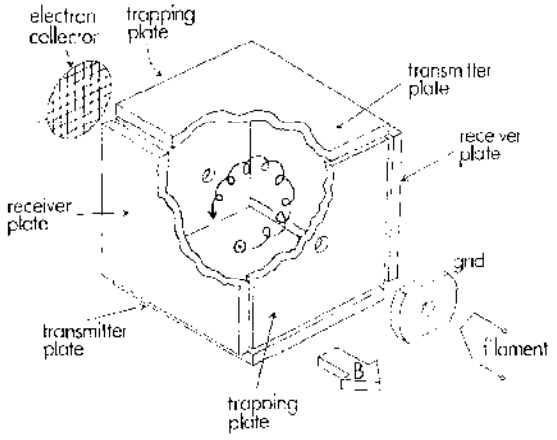


Fig. 2. FTICR/MS cubic analysis cell.

strong magnetic field (the Nicolet FTMS-1000 used in our work has a 3 T superconducting magnet). Ions can be formed in the cell from the low background pressure of an admitted sample by an ionizing electron beam passing through small holes in the trapping plates or by photoionization via irradiation through semitransparent grids in one or more plates (alternative ion sources are described in Section C.)

Application of an external oscillating electric field across the transmit plates at the characteristic cyclotron frequency of an ion causes ions of that mass in the cell to move into resonance with the applied field and spiral out to orbits of larger radius. The kinetic energy of the ion is given by $E_k = 2\pi^2 M \nu_c^2 r^2$, where r is the radius of the orbit. As the ions move into resonance with the applied electric field, their motion is shifted from having a random distribution of phases to that of all simultaneously moving in phase with the applied field as a "packet" of ions. If the applied field is turned off or moves out of phase with the ions, the ion packet persists long enough to induce an image current in the detect plates [27] before collisions with neutral molecules restore the initial random distribution of phases. The induced image current at the cyclotron frequency of the ion packet contains information in the time domain about the frequency (mass) of the ion, and the intensity of the signal produced is dependent on the ion population.

In order to detect simultaneously the masses and populations of many different ionic masses present in the cell, a fast radio-frequency sweep is applied to the transmit plates corresponding to the mass range of interest. As each ion of a particular mass moves into resonance, a superposition of image currents is generated in the detect circuit. The signal is amplified, digitized by an analog-to-digital converter and stored in a computer. The rapid sweep-and-detect cycle is repeated many times to improve the signal-to-noise ratio by signal averaging. The computer then performs a Fourier transform on the stored data. This mathematical procedure can analyze any complex time domain signal to present graphically a plot of amplitude vs. frequency (mass), thereby producing a mass spectrum. The high mass range is determined primarily by the magnitude of the magnetic field, with increasing resolution toward lower masses. A 3 T field yields good mass resolution up to approximately 3000 a.m.u. Thus the FTMS technique has the high resolution at large m/z values required to study many higher molecular weight metal complexes. An example is shown in Fig. 3 of a high resolution spectrum of the $Ru(hfac)_3^-$ molecular anion.

The lower mass limit is governed by the maximum rate of signal digitization. With a 5.2 MHz digitizer and a 3 T magnet, this limits the detectable masses to 17 a.m.u. and over. A lower magnetic field allows the detection of important lower mass ions such as OH^- with an accompanying decrease in high mass resolution.

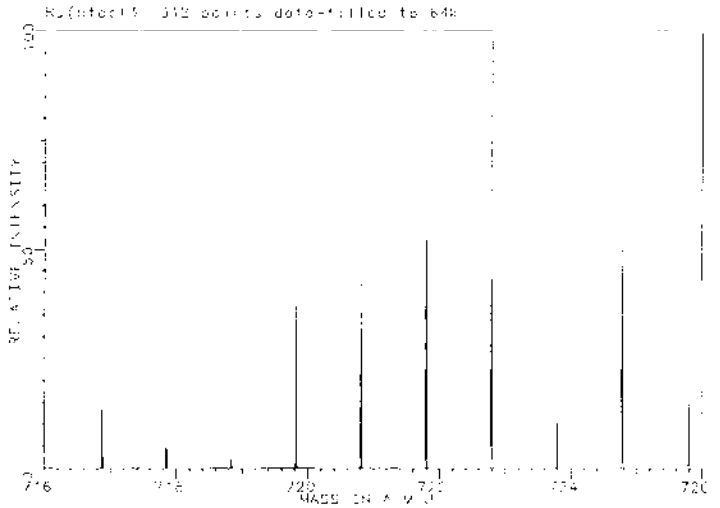


Fig. 3. High resolution mass spectrum of Ru(hfac)$_3$. Here 312 data points have been filled to 64k prior to the Fourier transform to demonstrate the high resolution capability of FTICR/MS.

(ii) Manipulations of ions in the trap

Between the ionization and detection events, any one ionic mass can be kinetically excited by application of a single-frequency pulse via the transmit plates. A range of masses can be excited by a frequency sweep. Selected ions can be ejected from the cell completely if they absorb sufficient energy to spiral out to orbits of such large radius that they strike the cell plates (ion ejection). If a low amplitude pulse or sweep is applied, the kinetic energy of the ions can be increased without ejecting them from the cell [28]. This technique can be used to explore endothermic reaction channels by increasing the energy of reactants, and this translational excitation is one way by which structural and thermodynamic information can be obtained. The kinetic energy of an ion can often be increased to the point that the excited ions fragment on collisions with neutral molecules to produce daughter ions in a process called collision-induced dissociation (CID), and this method can be a powerful method for the structure determination of ions [29,30]. Low energy CID can also be used to estimate the relative endothermicities of bond dissociative pathways if translational to vibrational energy transfer is of relatively constant efficiency.

An important factor contributing to the great versatility of FTICR/MS is that tailored pulse sequences can be applied in almost any combination.

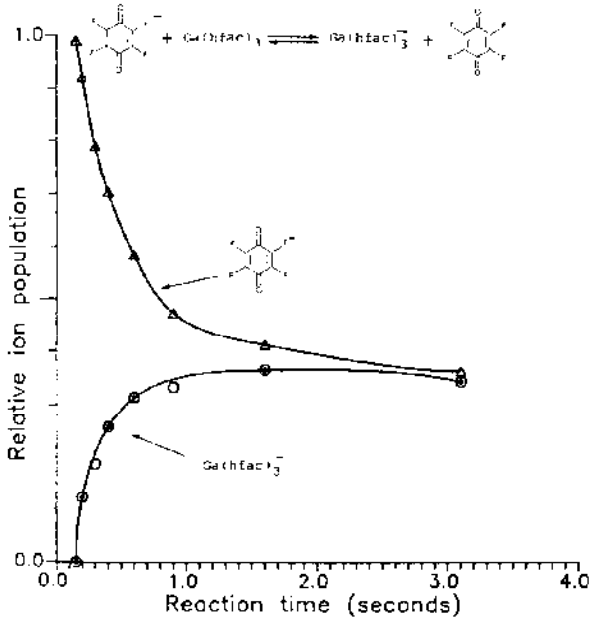


Fig. 4. Charge-transfer equilibrium between tetrafluorobenzoquinone and $Ga(hfac)_3^-$ anions and their neutrals is established approximately 3 s after ejecting $Ga(hfac)_3^-$ from the FTICR cell in a double-resonance experiment.

Thus subsequent excitation of daughter ions and even granddaughter ions (MS–MS) can be performed to extract further structural information all within the same analysis cell. Further, since a variable amount of time can be left between pulses the time-dependent appearance and disappearance [22] of ions can be monitored (Fig. 4). This feature enables rate constants to be obtained in the study of the kinetics of ion molecule reactions. At typical reaction pressures, the large excess of reactant neutral molecules (about 10^{13} cm^{-3} at 10^{-6} Torr) compared with the number of ions trapped in the cell (approximately 10^5 cm^{-3}) makes all second-order kinetics pseudo-first order. For ion–molecule charge-transfer reactions of low driving force (ΔG of a few kilocalories), equilibrium constants can be obtained by direct measurement of equilibrium ion populations at a known partial pressure of their neutral molecules. A significant limitation in kinetic studies arises from the finite trapping time of ions in the cell. We have obtained reliable kinetic data for reaction times up to approximately 30 s. Longer ion storage times can be achieved at reduced pressures, but of course this reduces the observed ion- neutral reaction rate proportionally.

The efficiency of a gas-phase reaction can be defined as the ratio of the observed rate constant to the estimated collision rate. The lower limit of measurable efficiency of a reaction in our FTICR/MS system is approximately 10^{-4}. Given that typical ion–molecule collision rate constants are in the range $(5–10) \times 10^{11}$ M^{-1} s^{-1}, this means rate constants of ca. 5×10^{7} M^{-1} s^{-1} or less are not easily determined. At first, such a limitation may seem severe; however, the absence of solvent often greatly accelerates many types of reactions, and the observable range is adequate for a wide variety of kinetic studies.

An important distinction between ICR and many other mass spectral techniques for the study of ion–molecule reactions is the potential for producing reactants at thermal energies rather than observing collisions between accelerated ions and thermal neutrals. The thermal condition can be approached by providing an unreactive collision gas as a buffer, thus increasing the number of thermalizing ion–molecule collisions prior to a potentially reactive collision. However, the assertion that truly thermal reactions can be studied in a standard ICR experiment is somewhat controversial; other specialized high pressure methods, such as flow tubes [31] and high pressure mass spectrometry [32], provide more rigorously thermalized ions for ion molecule studies.

C. SAMPLING METHODS FOR COORDINATION COMPOUNDS

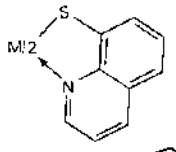
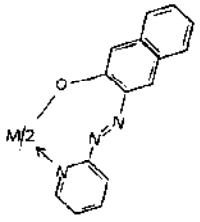
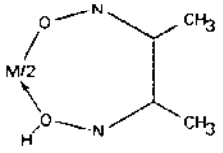
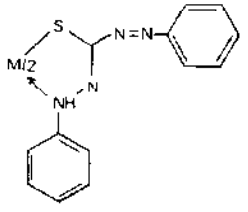
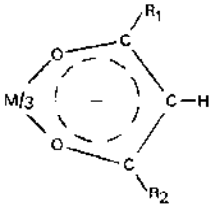
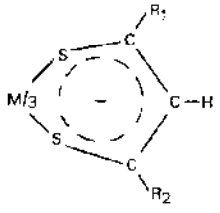
(i) Routine sample introduction

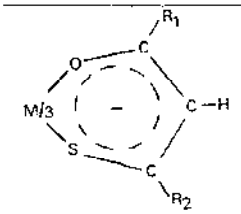
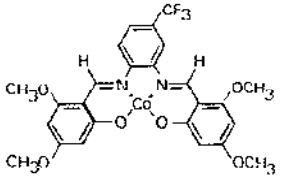
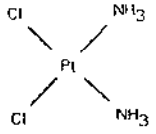
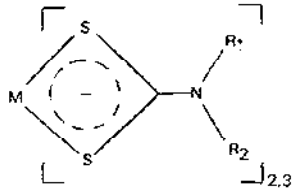
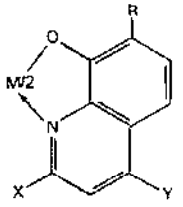
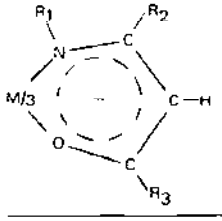
A typical FTICR/MS system is shown in Fig. 5. The main vacuum chamber containing the analysis cell is pumped by a large diffusion pump or turbomolecular pump. Total pressures of 10^{-9}–10^{-6} Torr are most commonly used. Samples can be admitted routinely by two methods. Gases and vapors from volatile liquids or solids are introduced via an inlet system through precision leak valves. Alternatively, for less volatile solid samples, a solids probe can be inserted through Teflon seals into the main chamber. The tip containing the sample can be electrically heated up to approximately 350 °C in order to produce a workable sample pressure. Introduction of coordination compounds by this method carries the general restriction that they must not be ionic as salts are too involatile. Table 1 lists a selection of coordination compounds from the literature, which have been successfully sublimed, suggesting the types of metal-containing compounds that can be admitted into the FTICR/MS by sample heating. The factors affecting the volatility of these compounds are discussed in the references cited [33–40].

Electron impact ionization of the vapor of a volatile coordination compound may not produce the molecular ion of interest. Fragmentation or

TABLE I

Volatile coordination compounds suitable for analysis by FTICR

Metal complex	Ligand	Ref.
	8-Mercaptoquinoline	33
	1-(2-Pyridylazo)-2-naphthol	33
	Dimethylglyoxime	33
	Dithizone	33
	2,4-Pentanedione $R_1 = R_2 = CH_3$ other derivatives and bis chelates	33–37
	4-Mercapto-3-penten-2-thione $R_1 = R_2 = CH_3$ and bis chelates also derivatives R_1 = phenyl, $R_2 = CF_3$	38

Metal complex	Ligand	Ref.
	4-Mercapto-3-penten-2-one $R_1 - R_2 = CH_3$ and bis chelates also derivatives R_1 = phenyl, $R_2 = CF_3$ $R_1 - R_2 = CF_3$	38
	Bis(4,6-dimethylsalicylidene)-4-(trifluoromethyl)-*o*-phenylenediimine (SALOPH)	40
	Also *cis*-platin and analogs	39, 40
	Diethyldithiocarbamate $R_1 = R_2 = C_2H_5$ and derivatives	33
	8-Hydroxyquinoline X, Y, R = H. Derivatives: X, Y = Cl or Br	33,34
	Tetraphenylporphyrin	33
	4-Anilino-3-pentene-2-one R_1 = phenyl $R_2 = CH_3$ $R_3 = CH_3$	33

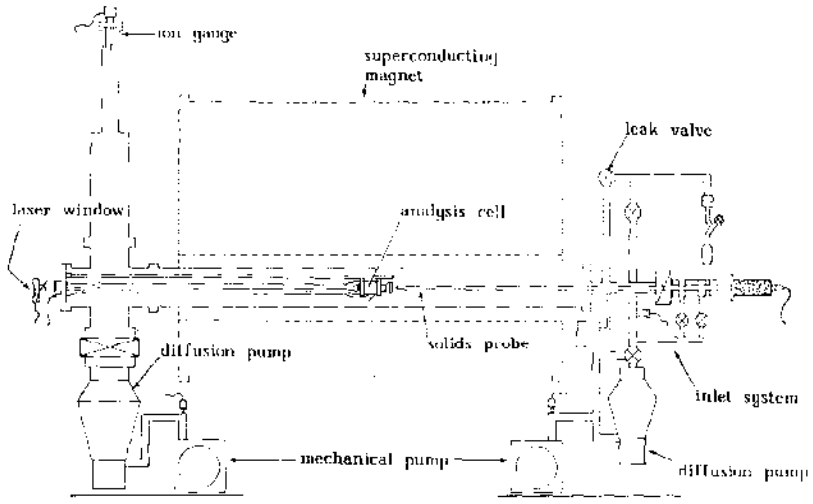


Fig. 5. Schematic diagram showing typical FTICR/MS components.

simple loss of one or more neutral ligands may accompany the ionization process. For example, the positive ion spectrum of the 50 eV ionization of *cis*-dichloro-*trans*-dihydroxobis(2-aminopropane)platinum(IV) results in the formation of various fragment ions [40]. However, a few hundred millisec-

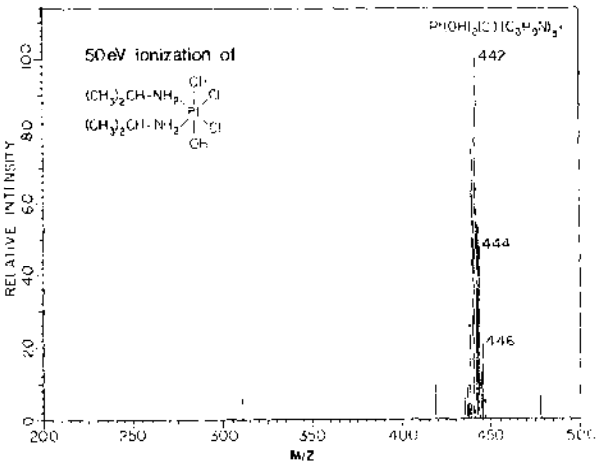


Fig. 6. Ion -molecule and charge transfer product of 50 eV ionization of *cis*-dichloro-*trans*-dihydroxobis(2-aminopropane)platinum(IV).

onds after the initial ionization, only one mass peak at 442 a.m.u. corresponding to the formula $Pt(OH)_2Cl(C_3H_9N)_3^+$ is observed (Fig. 6). The fragment ions initially produced undergo ion–molecule reactions and/or charge-transfer reactions with neutrals to produce the predominant peak at 442 a.m.u.

Fragmentation by electron impact to produce positive ions can be minimized by using a lower ionizing potential, which can be accomplished by reducing the electron beam accelerating voltage. Alternatively, chemical ionization (CI) of the sample vapor can be achieved by simultaneously ionizing an inert gas of higher ionization potential than the sample. Subsequent ionization of the sample neutrals by a charge-transfer reaction with ions of the added reagent may greatly minimize fragmentation compared with electron impact alone. In the production of stable negative ions, sufficient energy may be released to some molecules by the exothermic attachment of thermalized electrons that fragmentation becomes unavoidable. Here, alternative ionization methods such as CI may be essential to produce parent ions. For example, transition metal hfac complexes have been shown to fragment in a 70 eV electron beam in a conventional mass spectrometer to form various anionic fragments [41]. Similar fragmentation of hfac complexes has also been found in low energy electron attachment in FTICR/MS [42]. Fortunately, the neutral tris-chelate complex usually has a higher electron affinity than the fragment, and the molecular parent ion is observed a few hundred milliseconds after electron attachment as a result of electron transfer from the anionic fragments. Thus by waiting for completion of this chemical ionization process, good yields of the parent molecular ions are obtained for kinetic and thermodynamic investigations.

The low pressures at which the FTICR/MS operates makes introduction of low volatility samples such as coordination compounds quite practical, and the range of metal complexes that can be studied by simple sublimation has not been explored in great depth.

(ii) Laser desorption

An alternative method of introducing involatile samples into the FTICR/MS is by laser desorption [43,44]. Provision is made on the instrument to interface a laser trigger to the computer controlling the experimental pulse sequences. ZnSe windows can be mounted on the high vacuum chamber, and a special analysis cell is used to focus the beam inside the cell onto sample targets or onto the tip of a solids probe placed close to the cell. Typically, pulsed Nd:YAG, excimer or CO_2 lasers are employed with power densities of about 10^8 W cm^{-2}. Positive or negative ions are efficiently trapped from the desorbed plasma following the laser pulse. This

technique has the advantage of producing high molecular mass ions, often with little or no fragmentation. In the case of desorption using pure metal or alloy targets, bare metal cations, anions and clusters are produced [5,45,46].

Several reports in the literature describe the laser desorption of various types of compounds in mass spectrometry. For example, porphyrins [47], involatile organic compounds and salts [40,48,49] have been studied. Analysis of high mass biomolecules has been achieved by laser desorption [50]. The alkali metal ions form cationic (pseudomolecular) ions of the type $[M + K]^+$ or $[M + Na]^+$ (depending on whether a potassium or sodium salt is used), and instances are reported where a greater intensity of the molecular ion is observed than by FAB/MS. Rhodium complexes with various phosphorus donors of the type $Rh(PR_3)_2(CO)X$ where $R = C_6H_{11}$, C_6H_5, C_6F_5 and $X = F^-$, $SO_3CF_3^-$ and ClO_4^- have also been desorbed to produce M + K, M + Na, M^+, M–CO and M–X ion peaks [51]. The alkali ions probably come from desorbed ceramics in the FTICR/MS cell, but these problems can be minimized. The initial high pressure burst of desorbed neutrals following the laser pulse generally does not cause problems as it is quickly pumped away, leaving the ions trapped in the cell.

(iii) Alternative ion sources

The wide mass range and high resolution [22] of FTICR/MS makes it a powerful analytical tool. Coupling of conventional ion sources from various MS analytical techniques to the FTICR analysis cell offers the additional advantages of ion storage, signal averaging and soft ionization techniques in a single instrument. Problems are encountered owing to the low background pressure requirements for FTICR analysis. For example, the coupling of FTICR/MS to gas chromatography, fast-atom bombardment sources (FAB), electrohydrodynamic ion sources (EH) and liquid secondary ion sources (liquid SIMS) commonly used in conventional mass spectrometry has been hampered by the unacceptably high background pressures introduced by the gas chromatographic carrier gas or the liquid matrices. The advantage of these alternative ion sources is that they are "softer" methods of ionization than conventional electron impact. As a result, less fragmentation occurs upon ionization, thereby allowing parent ion molecular weight determinations or the introduction of intact molecular ions for ion–molecule reaction studies. The advantages of FTICR/MS analysis have prompted considerable effort over the last decade to incorporate these soft ionization methods into the FTICR/MS technique. Although in an early stage of development, this work is broadening the range of compounds that can be studied by using FTICR/MS. The advantages of subsequent ion manipulation or

photochemistry of the trapped ions hold the potential for the determination of kinetic and thermodynamic data of thermally fragile, involatile compounds such as large biomolecules or coordination complexes.

As outlined above, one of the most common routine soft ionization methods is laser desorption. Since solid samples are used, no problems arise from high background pressures. Similarly, in static SIMS [52], involatile solid samples can be desorbed and analyzed directly in the FTICR high vacuum chamber by bombarding the sample with a beam of high energy (ca. 4 keV) cesium ions. Static SIMS is a feature of the commercially available Spectrospin CMS47 FTICR mass spectrometer [53].

Considerable work has also focused on coupling high pressure sources to the FTICR experiment. The general solution to the problem is to generate ions externally in a higher pressure source and transfer them into the lower pressure FTICR analysis cell, which is isolated from the high pressure region by conductance limits and pumping. A particularly elegant example of this high and low pressure chamber configuration is seen in the coupling of gas chromatography to FTICR mass analysis. A dual analysis cell has been developed by Nicolet Analytical Instruments specifically for this purpose [54] and is commercially available on the FTMS-2000 spectrometer. In the dual-cell configuration, a source cell located in a differentially pumped high pressure chamber (10^{-6}–10^{-5} Torr) is connected to an analyzer cell in a low pressure chamber (10^{-9}–10^{-8} Torr) by a central trapping plate common to both cells. Mass analysis can then be performed by transferring ions formed in the high pressure cell to the low pressure analyzer cell.

External ion generation by particle bombardment of involatile samples in a glycerol matrix in an external high pressure source (FAB and liquid SIMS) has also been used successfully in conjunction with FTICR/MS analysis [55]. Inclusion of a quadrupole mass filter enables mass selection of the ions prior to trapping in the FTICR cell in the low pressure chamber [56].

Field desorption (FD) [57] is an even softer method of ionization. In the FD source a solution containing the analyte is loaded onto an emitter wire. Desorption and ionization are achieved by heating the emitter wire in a high electric field. Coupling of FTICR/MS with FD is readily achieved [58] since there is no pressure increase associated with ion generation. A disadvantage of FD compared with particle bombardment sometimes arises with samples of low thermal stability since the emitter may have to be heated to several hundred degrees to produce sufficient ion emission. Bursey and coworkers have studied the mass spectrometry of coordination compounds and organometallics by using fast-atom bombardment and field desorption ion sources [59]. Several complexes of rhodium, rhenium, osmium and molybdenum containing 1,5-cyclooctadiene, carbon monoxide and various nitrogen, sulfur, and phosphorus donor ligands [60] and also copper(I) and

copper(II) complexes of monodentate and multidentate *N*-heterocyclic ligands [61] were used in a comparison of the two ionization methods for analytical purposes. FD was found to be a better method to produce intact cations from both neutral complexes and salts of 1+ cations. Solution phase ligand lability was paralleled by analogous ligand loss in the gas phase and the ionic fragments produced could be related to solution substitution chemistry of many of the complexes studied. Although conventional mass spectral analysis was used, the work serves as an illustration of the types of inorganic ions that can be generated by these methods for possible FTICR ion manipulation and analysis.

Electrohydrodynamic mass spectrometry [23,62,63] shows promise as an application of mass spectrometry to probe solution and gas-phase chemistry of coordination compounds. For ionic compounds the ionization event occurs in a polar solution (usually glycerol containing an electrolyte). The ions can be sampled directly from solution by the action of an applied electrostatic field. Hence ions generated in solution are directly transferred into the gas-phase ion source. For glycerol solutions of $[Ru(bpy)_3]^{2+}$ and $[Cr(bpy)_3]^{2+}$ with added sodium chloride, Chan and Cook [23] showed that the ruthenium complex formed only the parent dication peak at $m/z = 285$ (full width). The chromium complex, which is labile to ligand exchange in solution, produced peaks of mass and isotopic distribution ratio corresponding to loss of a bipyridyl ligand and substitution of chloride ions and solvent molecules, suggesting that ligand exchange had occurred in solution. Later modification of the ion source permitted the use of volatile solvents including water [64]. The potential utility of this mass spectral technique in the study of ligand exchange processes in solution and in the production of gas-phase ions with solution counterparts is apparent.

D. APPLICATIONS IN GAS-PHASE COORDINATION CHEMISTRY

(i) Determination of adiabatic ionization potentials and electron affinities

ICR and other gas-phase techniques can be used to determine adiabatic ionization potentials and electron affinities of neutral compounds via bracketing or equilibrium methods. For ionization potentials, the reactions studied in these investigations are of the general type given in eqn. (1), where

$$ML_n^+ + X \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ML_n + X^+ \qquad K_1 \qquad (1)$$

ML_n represents an organometallic or coordination compound and X is either another metal-containing molecule or a non-metallic electron donor

compound. In thermal energy reactions, if the forward reaction of eqn. (1) proceeds and the reverse does not, the process can be assumed to be exoergic and the relative order of the aIP values is deduced. If the reverse process proceeds with X replaced in eqn. (1) by a species Y, the aIP of the metal complex is then bracketed between the known values for X and Y. In some cases, the equilibrium constant K_1 can be directly determined from the neutral pressures (of X and ML_n) and the ion population of the cell at long trapping times. Relative EA values can be obtained via completely analogous procedures applied to the reaction of eqn. (2):

$$ML_n^- + X \rightleftharpoons ML_n + X^- \qquad K_2 \qquad (2)$$

Applications of these techniques to many organic compounds have been described [65,66], but little has been done with metal-containing complexes.

The electron affinities or ionization potentials of the reference compounds X in eqns. (1) and (2) can be obtained by equilibrium bracketing with compounds for which the aIP or EA values have been reliably determined by other methods. For example, Keharle and coworkers have bracketed electron affinity values for approximately 100 organic compounds by this method, covering a range from approximately zero to about 3 eV [66,67]. The reference compound is SO_2, for which the electron affinity has been accurately determined by Hall and coworkers to be 1.097 eV by photoelectron spectroscopy [68]. By observing the effect of temperature on the electron-transfer equilibria established between successive compounds in a free energy "ladder", Van't Hoff plots were produced [69] which lead to ΔH and ΔS data. Relating the ΔH data to that between the unknown compound and SO_2 yields an estimate of the electron affinity of the unknown. The results are in good agreement with electron affinities of some of the same compounds determined in a similar investigation using FTICR/MS [70].

Transition metal hexafluorides are quite volatile and have been studied by using a variety of gas-phase techniques. Much of the interest in these compounds apparently arises from the importance of UF_6 in nuclear chemistry and the strongly oxidizing character of many $M(VI)F_6$ complexes [71]. Electron affinity is the fundamental property of direct relevance to oxidizing tendencies [67]. Many methods have been used to determine EA values for MF_6 complexes, including ICR/MS. George and Beauchamp [72] derived an EA value for WF_6 of $3.5 + 0.1$ eV by observing charge transfer from F^- but not from Cl^-. They were further able to show that translational excitation of Cl^- opened a charge-transfer channel, suggesting that the failure to observe electron transfer at thermal energies was due to an activation barrier or endothermicity. Later, more extensive studies by Viggiano et al. [73], using ion flow tube methods, set the EA value as $3.36(+0.04$ and $-0.2)$ eV. Although considered unlikely by the latter authors, the actual ground state

EA value could be higher if the ion–molecule methods produced an excited electronic state of WF_6^-.

The possibility that a significant activation barrier is present for less exoergic charge-transfer reactions $X^- + WF_6$ cannot readily be discounted, however. George and Beauchamp [72] reported a rather low rate constant for the F^- (EA = 3.40 eV) reaction, suggestive of an intrinsic Franck–Condon barrier to the WF_6/WF_6^- interconversion. Viggiano et al. [73] found the Br^- (EA = 3.36 eV) charge transfer to WF_6 to be near collisional, suggesting no significant intrinsic barrier. In work relevant to this issue, Kebarle and coworkers [74] found gas-phase electron-transfer reactions of SF_6^- to become increasingly inefficient as the exoergicity decreased. As shown by Richardson [75], this effect can be explained through simple theoretical arguments relating a large intrinsic activation barrier for the SF_6/SF_6^- interconversion to the rates of cross-reactions. The electron self-exchange rate for SF_6/SF_6^- is immeasurably slow by FTICR/MS [76]; a similar experiment for WF_6/WF_6^- would reveal any intrinsic barrier for that couple and clarify the issue of the EA of WF_6.

As mentioned in Section C, transition metal hfac complexes have been observed to form stable parent molecular anions by electron attachment to the neutral compound [42]. This attachment almost certainly corresponds to a reduction of the metal center from M(III) to M(II) for the d^0 to d^9 M(III) centers. The electron-transfer equilibrium data of Kebarle have been used to estimate the EA values for these transition metal compounds [42]. This study provides insight into the factors affecting the oxidation potentials of various trivalent first row transition metal complexes with a pseudooctahedral ligand field (D_3 symmetry). The relative order of the electron affinities of the series of first row transition metal tris-chelate complexes was determined to be Ga < Sc < Cr < Ti < V < Fe < Co < Mn. The magnitudes of the electron affinities were found to be in the range from 2.6 to greater than 3.2 eV, with a few coming to equilibrium with organic acceptors [42] (Fig. 4). The absence of complicating solvation effects enables comparisons with the results of theoretical calculations, and the relative importance of exchange interactions, *d*-orbital degeneracies, spin pairing and nuclear charge in determining reduction potentials can be evaluated [42].

The determination of adiabatic ionization potentials can be obtained by studying gas-phase reactions of cations exactly analogous to those described above. Such determinations will be of fundamental importance in compiling the thermodynamic properties of metal complexes since photoionization and photoelectron methods yield vertical ionization potentials, and transitions to the ground vibrational level of the ion state are usually not readily identified in the typically broad spectral manifolds [1].

(ii) Kinetics of electron-transfer reactions

Studies of electron-transfer phenomena have usually considered either atoms and small molecules (containing a few atoms) in the gas phase [76–84] or large polyatomic molecules in solution [85–87]. Few researchers have carried out extensive investigations of the kinetics of gas-phase electron transfer involving large polyatomic reactants [42,75,76,88–92], and, until recently, little had been done with metal-containing compounds. Such investigations bridge the gap between the two reaction types mentioned and can potentially provide insight into the role of solvent in determining the kinetics and thermodynamics of condensed-phase reactions. We have recently reported FTICR/MS studies of the kinetics and thermodynamics of electron-transfer reactions of organometallic and coordination compounds in the gas phase [75,76,88,89]. In some cases, reactions with direct solution counterparts have been studied in the gas phase; thus the unusual opportunity arises to compare the reactivities of metal-containing molecules in the presence and absence of solvent.

The ability to follow the ion population of the ICR trap as a function of time makes determination of gas-phase electron-transfer reaction rates by FTICR/MS relatively convenient. When $X = ML_n$ in eqns. (1) or (2), the familiar case of the self-exchange reaction applies. When X is a different donor or acceptor, cross-reactions can then be studied. It should be noted that dissociative charge transfer is not usually encountered in thermoneutral or near-thermoneutral charge-transfer ion–molecule reactions of large polyatomic reactants, i.e. no bond breaking occurs as a result of the electron-transfer event. Experimentally, ions are prepared in the ICR trap by the methods described above, and the pressure of neutrals is adjusted so that the time dependence of the trap's ion population can be conveniently followed on the reaction time scale. In a few cases, eqns. (1) or (2) come to equilibrium, and both k_f and k_r can be obtained [42,76] (Fig. 4).

The technique of FTICR ion ejection is commonly employed to determine the rate constants of self-exchange reactions. For most large polyatomic molecules, especially for those containing transition metals, several isotopes exist with at least 10% natural abundance. One or more of these isotopes can usually be efficiently ejected in the presence of the others. For high molecular weight ions, ejection to 1 a.m.u. resolution is sometimes experimentally difficult, but this limitation can be overcome by isotopic enrichment of the samples. As the non-ejected ions charge-transfer to neutrals after the ejection pulse, the self-exchange reaction may be monitored by following the reappearance of the ejected ion mass(es) with time. This technique can be applied equally readily to reactions involving cations or anions in eqns. (1) and (2). Figure 7 illustrates the method applied to the $[Ga(hfac)_3]^{0/-}$

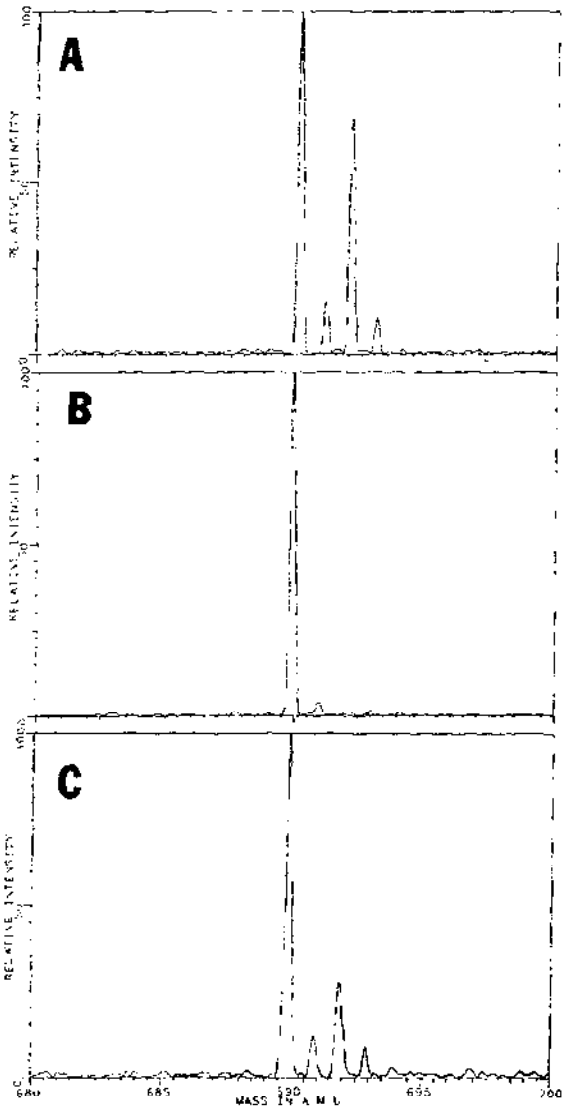


Fig. 7. Double-resonance ion ejection applied to $Ga(hfac)_3^{-0}$ self-exchange reaction. Spectrum A shows the natural distribution of isotopes present in the complex. The two main peaks arise from the ^{69}Ga (60%) and ^{71}Ga (40%) natural isotopes. The two smaller peaks are due to natural ^{13}C. B shows the ion signal after ejection of the ions with m/z values of 692 and 693 a.m.u., and C shows the partial reappearance of the ejected peaks 5 s later.

TABLE 2

Selected rate constants for gas-phase electron transfer reactions

Reactants	k_f (cm^3 s^{-1}) [a]	Est. eff. (k_f/k_{coll}) [b]
Self-exchange reactions		
Cp_2Fe (0/−)	2.7×10^{-10}	0.27
$Cr(CO)_6$ (0/+)	2×10^{-10}	0.15
Cp_2Mn (0/+)	1.3×10^{-11}	0.013
$(MeCp)_2Mn$ (0/+)	4.2×10^{-11}	0.040
$(Me_5Cp)_2Mn$ (0/+)	3.1×10^{-10}	0.28
SF_6 (0/−)	$<5\times10^{-14}$	<0.0001
$Ru(hfac)_3$ (0/−) [c]	3.0×10^{-14}	0.03
$Cr(hfac)_3$ (0/−) [c]	7×10^{-14}	0.07
Cross-reactions		
Cp_2Mn/Cp_2Fe^+	5.0×10^{-10}	0.5
Cp_2Mn/Cp_2Ni^+	3.1×10^{-11}	0.03
Cp_2Ni/Cp_2Mn^+	1.3×10^{-11}	0.013

[a] Error estimated as 30%; temperature ca. 375 K; data from ref. 76 except where indicated. [b] Estimated efficiency, defined as the ratio of k(forward)/k(collision), where the collision rate is estimated by the Langevin rate constant. [c] See ref. 42.

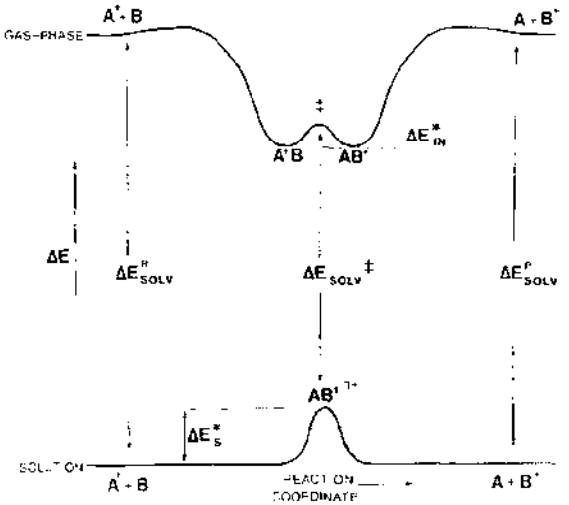


Fig. 8. Qualitative comparison of potential surfaces for solution and gas-phase charge-transfer reactions. In the gas phase, conversion of the precursor complex (A^-B) to successor complex (AB^-) involves a reorganizational barrier ΔE^*. In solution this intrinsic barrier is often masked by larger barriers owing to solvent reorganization. In addition, stabilities associated with the precursor and successor ion–neutral complexes are significantly reduced by solvent effects. Charge-transfer reactions in solution are typically orders of magnitude slower than those for the same reactants in the gas phase [76]. Note that the overall exoergicity of the reaction can also change in going from the gas phase to solution owing to differences in solvation energies of reactants (ΔE^R_{solv}) and products (ΔE^P_{solv}).

self-exchange reaction. In our work [76], rate constants are obtained by following the mole fraction of the ejected ion, obtained from ratios of the peak areas with time. This alleviates most problems arising from non-reactive ion loss and the effects of instrumental fluctuation. Cross-reactions can be followed in a similar manner and provide an opportunity to study the effect of exoergicity on the electron-transfer rates [42,76].

An indication of the potential for direct comparisons of the gas phase and solution is seen in our work on electron-transfer reactions of metallocenes and other organometallic species [76]. The same methodology is currently being applied to electron-transfer reactions of coordination complexes such as $[M(hfac)_3]^{0/-}$ [42]. A selection of results for self-exchange and cross-reactions is presented in Table 2. For example, the self-exchange rate constant at 375 K for $[Ru(hfac)_3]^{0/-}$ is found by FTICR/MS to be 3×10^{-11} cm^3 s^{-1} (2×10^{10} M^{-1} s^{-1}), while the same reaction has a rate constant of 5×10^6 M^{-1} s^{-1} at 298 K in acetonitrile [93]. Thus, since removing the solvent increases the rates of this electron-transfer process by a factor of ca. 5000, this result is a dramatic direct illustration of the extent to which charge trapping by the solvent contributes to the barriers to electron transfer in solution (Fig. 8).

(iii) Ligand substitution reactions

The subject of the kinetics of ligand substitution reactions at metal centers is among the most intensively studied topics in coordination chemistry. Essentially all this work has been done for complexes in solution [94–96]. It is of interest to consider whether the bond energies and ligand substitution kinetics for gas-phase complexes can be determined to provide insight into how solvation affects these processes. In addition, gas-phase data more directly reflect the intrinsic metal–ligand bonding than do solution studies, where solvation of reactants, transition states, and products can significantly influence thermodynamics and kinetics. Several studies, many cited by Allison in his review [17], demonstrate how such reactions can be followed in the gas phase. For example, Corderman and Beauchamp [97] determined the relative affinities of 30 bases for the cation $(C_5H_5)Ni^+$ by using the ICR/MS equilibrium method for reactions of the type shown in eqn. (3):

$$(C_5H_5)Ni(B)^+ + B' \rightleftharpoons (C_5H_5)Ni(B')^+ + B \qquad (3)$$

The authors suggest that the equilibration is rapid owing to the coordinatively unsaturated nature of $(C_5H_5)Ni(B)^+$, which is a 16-electron species. Thus the ligand exchange mechanism was suggested to be associative.

No direct comparisons of gas-phase and solution ligand exchange reactions at metal centers in ion–molecule processes have been reported. Such comparisons are certainly possible in principle given the wide range of compounds that can be studied under both conditions. It is of interest to consider the possibilities for associative and dissociative pathways in gas-phase chemistry at metal centers. Associative mechanisms will be most likely for larger metals in coordinatively unsaturated complexes (as in the case of the $(C_5H_5)Ni(B)^+$ chemistry above). The possibility that 18-electron coordination complexes may exchange ligands readily via an associative pathway in the gas phase should not be dismissed, especially for weak ligand field donor complexes (e.g. the solution chemistry of 18-electron Rh(III) ammines is suggestive of associative mechanisms for ligand substitution [98]). However, dissociative pathways may arise in the gas-phase chemistry when the ion–molecule interaction chemically activates [99,100] the collision complex toward dissociation of a weakly bound ligand. Chemical activation arises from stabilization of the collision complex (precursor complex), which is bound by ion–dipole, ion-induced dipole, or other types of interactions.

The kinetics of gas-phase ligand substitution reactions at metal centers have received little detailed attention. This is obviously an area that will have its own unique features as well as a potential for contributing to our understanding of solution chemistry.

(iv) Gas-phase ligation of metal ions

The stepwise ligation of metal ions in the gas phase is represented by the equilibria of eqn. (4):

$$[M(L)_{n-1}]^+ + L \rightleftharpoons [M(L)_n]^+ \quad (n = 1, 2, 3 \ldots) \tag{4}$$

The sequential binding of bases such as NH_3, H_2O and CH_3CN to a number of metal ions (e.g. alkali metal ions, Pb^+, Sr^+ [101], Cu^+ [102]) has been studied by high pressure MS and by ICR methods, and binding enthalpies have been determined in many cases. Generally speaking, the association between the closed shell cations and bases can be well described by an electrostatic model, and little electron density transfer to the metal ion is expected. The enthalpy of association becomes less exothermic as n increases, in agreement with theory [103]. Since the addition of a ligand is exothermic, the excess kinetic energy released upon binding in the gas phase must be dissipated via third-body collisions with buffer gas molecules or a second ligand molecule. In contrast to these gas-phase processes, ligation in solution occurs in a thermal bath and almost invariably involves displacement of solvent from the inner coordination sphere.

It would be of interest to study the analogous equilibria of eqn. (4) for open *d*-shell transition metal ions. Effects of ligand field stabilization in various possible geometries might appear in the stepwise enthalpies of ligand binding. The prospects for studying ligand binding by ICR methods for higher charged ions, e.g. M^{2+}, seem poor for typical ligands and transition metals since the second ionization potentials for the metals tend to be several electronvolts higher than the first ionization potentials of common neutral ligands such as amines.

(e) Other applications

We will conclude our discussion of applications by mentioning two promising areas for future study of coordination compounds in the gas phase by FTICR techniques.

Gas-phase Bronsted acidities and basicities of many organometallic complexes have been determined by the use of ion–molecule techniques, including ICR/MS. These include acidities of metal hydride complexes [104] such as $HMn(CO)_5$ [105] and the basicities of neutral 18-electron complexes [106]. In addition, the thermodynamics of bond cleavage for many bare metal hydrides, MH, have been investigated [8,107]. These studies have made use of extensive gas-phase proton affinity and basicity scales determined for a large number of acids and bases [108]. In principle, the same methods can be applied to study the acidity or basicity of coordinated ligands. For example, the acidity of aquo complexes is highly dependent on the nature of the metal ion and other coordinated ligands. The gas-phase acidity of aquo complexes could be studied via equilibria of the type in eqn. (5):

$$L_nM{-}OH_2 + B \rightleftharpoons L_nM{-}OH + BH \qquad (5)$$

where the basicity of the reference bases B is known. In a similar manner the basicity of neutral complexes could be obtained via equilibria of the type in eqn. (6):

$$L_nM{-}X + YH^+ \rightleftharpoons L_nM{-}XH^+ + Y \qquad (6)$$

where X is a relatively basic ligand such as an oxide or hydroxide. In the latter class of reactions, the site of protonation may not be readily deduced.

The coupling of lasers to FTICR/MS opens a vast wealth of possibilities for fundamental studies of bonding, structure, and photoreactivity in gas-phase metal complex chemistry. In addition to the application of lasers to desorption methods described earlier, trapped ions can be vibrationally excited with IR lasers or electronically excited with UV and visible laser sources. Absorption of many photons can occur prior to thermalizing

collisions with neutrals, thereby depositing large amounts of energy into the ion. In the case of IR multiphoton dissociation (IR–MPD) [109–111], sufficient energy can be built up in the ion to break a bond(s). Since vibrational energy is rapidly randomized throughout the available degrees of freedom [99,100], the first bond to break is usually considered to be the weakest. Thus IR–MPD can be a powerful probe of structure and bonding. For example, Watson et al. [40] have applied IR–MPD in a mass spectrometric study of the platinum complex ion in Fig. 6 and a cobalt Schiff base. For studies of reactivity at metal centers in the gas phase, IR–MPD may be a convenient method of introducing coordinative unsaturation in metal complex ions [109–111].

Irradiation of gas-phase metal complex ions into visible and UV absorbance bands can also lead to photodissociation of ligands. Fukuda and Campana have described photodissociation experiments for a large number of metal β-diketonate ions [37], and Dunbar has described those for metalloporphyrin ions [112]. In another type of process, photoionization of neutrals can occur by multiphoton ionization (MPI) [113] if the photon energy is sufficiently high (UV or visible). The ionization is usually accompanied by dissociation of one or more bonds to produce a fragment ion. MPI studies on metal compounds are relatively scarce and have been reported only for organometallic species such as metal carbonyls [114], metal arenes [115] and metallocenes [116–119]. The predominant observation in these studies is production of the bare metal ion, M^+, following complete photolysis of the ligand–metal bonds. MPI of coordination complexes has only recently been reported [120] and clearly deserves further investigation.

E. CONCLUSIONS

The study of coordination compounds in the gas phase is evidently a subject with broad significance in the further development of our understanding of the thermodynamics and reactivities of metal complexes. The work summarized in this review serves to suggest the large number of relevant and informative types of experiments that have not yet been performed. The area seems limited only by our ingenuity in devising new chemical and instrumental approaches to answer the questions which arise.

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