Determining Bond Strengths and Dissociation Dynamics of Diatomic Metal-Containing Ions by Photofragment Imaging

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DETERMINING BOND STRENGTHS AND DISSOCIATION DYNAMICS OF DIATOMIC METAL-CONTAINING IONS BY PHOTOFRAGMENT IMAGING

A Dissertation Presented

by

SCHUYLER P. LOCKWOOD

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Department of Chemistry
DETERMINING BOND STRENGTHS AND DISSOCIATION DYNAMICS OF DIATOMIC METAL-CONTAINING IONS BY PHOTOFRAGMENT IMAGING

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ABSTRACT

DETERMINING BOND STRENGTHS AND DISSOCIATION DYNAMICS OF DIATOMIC METAL-CONTAINING IONS BY PHOTOFRAGMENT IMAGING

FEBRUARY 2023

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Studies of simple metal ion – ligand complexes have primarily focused on understanding their roles in activating C-H and C-C bonds. However, data are often lacking on the fundamental properties of these species, which can have unusual bond orders and cluttered electronic structures with many states of multi-reference character, complicating their treatment in theoretical studies. Experimental work determining high-precision bond energies, ground state identities and excited state dynamics of a wider variety of metal-containing ions is needed to establish a robust set of well-characterized benchmark molecules. This work describes studies of the energetics and dynamics of several MX\(^+\) species, NiO\(^+\), NiS\(^+\) and MgI\(^+\), by photofragment ion imaging, photodissociation spectroscopy and theory. These systems each have properties that make them challenging for spectroscopic methods alone; however, imaging their fragments provides key context to their spectra, enabling in-depth analysis. NiO\(^+\) shows weak absorption near its bond dissociation energy and a broad and featureless photodissociation spectrum. However, imaging its photoproducts reveals that, at a much higher photolysis energy of \(~29000\) cm\(^{-1}\), a dramatic shift occurs in the preferred dissociation pathway from formation of ground state Ni\(^+\) + O to electronically excited Ni\(^{++}\) + O products. Image anisotropy and the results of MRCI calculations suggest NiO\(^+\) photodissociates via a parallel 3
4Σ− ← X 4Σ− transition above the Ni+* threshold, and via overlapping parallel and perpendicular transitions to several 4Σ− and 4Π excited states at lower energy below the Ni+* threshold. In contrast to NiO+, NiS+ absorbs strongly at its bond dissociation energy (~20000 cm⁻¹), resulting in a highly structured photodissociation spectrum. Analysis of the spectrum is complicated by the plethora of predicted transitions in the region, the presence of suspected hot bands, and uncertainty in the identity of the ground state. In this case, observation of parallel anisotropy in the images of Ni+ (2D) photofragments is key to assignment of the ground state and the dominant electronic transitions (3, 4 and 5 4Δ ← 1 4Δ), while the kinetic energy release (KER) distributions of images near the dissociation onset confirms the two lowest-energy peaks in the spectrum are due to hot ions. Finally, MgI+ is the most spectroscopically challenging of the three molecules, despite absorbing strongly near both its ground and excited state product thresholds. In fact, absorption via the most intense transition ((3) Ω=0+ ← (1) Ω=0+; 33000 to 40000 cm⁻¹) does not result in dissociation to the expected ground electronic state Mg+ + I products, likely due to rapid, efficient fluorescence. Instead, despite being energetically forbidden, excited charge transfer (Mg + I+) photoproducts are observed. The KER distributions of I+ fragment images show that the observed fragment channels result from resonance enhanced two-photon dissociation. This is the first reported direct observation of REPD of a molecule in which this photolysis process was not already known to occur. Finally, the KER distributions give high-precision bond dissociation energies: $D_0$ (MgI+) = 203.0 ± 1.8 kJ/mol, $D_0$ (NiS+) = 240.3 ± 1.4 kJ/mol, and $D_0$ (NiO+) = 244.6 ± 2.4 kJ/mol.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Energetics and dynamics of metal ion - ligand interactions underly inorganic and organometallic chemistry, from systems of isolated gas-phase molecules to bulk structures such as heterogenous catalysts. In the former size regime, for example, reactions of gas-phase diatomic metal – containing ions (MX+) with hydrocarbons are simple models for C-H and C-C bond activation.1-3 These reactions are highly relevant to goals of industrial catalysis, such as methane (natural gas) to methanol conversion for efficient storage and production of commodity chemicals from hydrocarbon feedstocks. Gas-phase MX+ show rich chemistry with alkanes, other organic compounds, and small molecules that varies with the classification of the metal (s, p, d – block) and non-metal (group IV, chalcogenide, halide, etc.); many of these reactions involve dissociation of the M+ – X bond to form the observed products.4-7 Bonds to metal cations can involve both covalent and electrostatic interactions; understanding the (sometimes unusual) nature of chemical bonding in MX+ is crucial for accurate theoretical treatment and experimental measurement of these catalytic reactions. Yet, experimental information on the fundamental properties of MX+ is often accompanied by large uncertainty, and for some species there is little to no reported data. This lack of detailed, high-precision data further complicates the assessment of theoretical predictions.
1.2 Metal-Containing Ions: Bond Strengths

Refining a bond strength measurement for just one molecule can substantially improve our understanding of complex systems with many bonds and intermolecular interactions. Theorists rely primarily on accurate and precise experimentally measured bond dissociation energies ($D_0$) to evaluate the accuracy of their calculations in the development of cost-effective density functionals. Unfortunately, measured $D_0$ values can depend significantly on the experimental method used, and different reports for the same species sometimes do not even agree with each other. Further, the experimental uncertainties in $D_0$ values for metal-containing ions ($\pm \sim$6-15 kJ/mol) are usually very large compared to those for non-metal species and fall well short of desired chemical accuracy ($\pm$ 4 kJ/mol). Using many different techniques to make these measurements thus ultimately makes convergence on a reliable, accurate value more likely.

Bond energies in metal-containing systems, as well as many non-metal species, have historically been measured by collision induced dissociation (CID, by crossed ion beams or guided ion beams), ion-molecule reactions (IMR, of thermalized ions, or in guided ion beams), or photodissociation onset (by photolysis of ion beams). These are all powerful and versatile techniques that can be used to measure thermodynamics in a wide array of chemical species. However, in certain cases, each has disadvantages. The first two techniques, which rely on collisions between molecules and/or atoms to break bonds, give an overestimate of $D_0$ if the system has too few excited states at energies near $D_0$ (for CID) or if there is a barrier to the ion-molecule reaction that exceeds $D_0$ (for IMR). Measuring a photodissociation onset also gives an overestimate of $D_0$ if there are too few proximate excited states, but can conversely give an underestimate if the onset is a hot band. Each of
these techniques thus suffers from supplying more energy to the system than is needed to break the bond without indicating how much energy to “subtract off.” What is not observed in these experiments is that the products formed carry away the excess energy as internal and/or kinetic energy following dissociation. Internal energy can be distributed in excited electronic, vibrational, and rotational quantum states. How excess energy is distributed to the fragments depends on the bound molecule’s excited state, propensity for coupling to nearby states, and which products each state correlates to. To give context to experimentally measured bond energies, it is therefore useful to concurrently examine the system’s electronic structure and predicted dynamics.

1.3 Metal-Containing Ions: Electronic Structure and Dissociation Dynamics

Understanding chemical bonding requires a detailed knowledge of electronic structure; this is especially important for transition metal-containing systems. These molecules often have many low-lying electronic states, unpaired electrons, multiple ground state electron configurations and significant spin-orbit effects. Effects can be negligible, with potential energy curves (potential energy of a quantum state as a function of bond length) well-described by the quantum numbers contained in standard term symbols for diatomic molecules. However, with sufficient spin-orbit splitting, for example, total angular momentum is the only meaningful quantum number.\(^8\) Even with less splitting, the energetic order of electronic states can change if potential energy curves are calculated with inclusion of spin-orbit effects. This makes it difficult to reliably predict electronic structure, bond energies and excited state dynamics without performing very high-level ab initio calculations. On the other hand, these more expensive computational methods are
crucial for predicting how $\text{MX}^+$ move along and between their potential energy curves. The complex dynamics that often occur in these systems, such as non-adiabatic coupling, are challenging current areas of research in theoretical chemistry.$^{9,10}$ and corresponding data from experiment are needed to evaluate predicted behavior.

Traditional spectroscopic methods (measuring absorption or fluorescence) can provide experimental insight into electronic structure near the Franck-Condon region. However, $\text{MX}^+$ often do not strongly absorb or fluoresce, so these techniques are not as powerful for these systems as for those with strong light-matter interactions. Rather, upon absorption of a photon (usually in the visible or near UV) $\text{MX}^+$ can photodissociate; this process depends on the electronic structure and dynamics both near and far from the Franck-Condon region.

1.4 Photofragment Velocity Map Imaging

Measuring the bond strength, electronic structure, product kinetic energy and product internal quantum states in one experiment would give a near-complete picture of bond dissociation along a molecule’s potential energy surface. Ion photofragment imaging,$^{11}$ specifically velocity map imaging (VMI),$^{12}$ is likely the closest thing to this “ideal” experimental technique. Since a group of newly formed fragment ions with some kinetic energy is roughly an expanding sphere of charges, accelerating the sphere at an imaging detector gives a two-dimensional projection of the fragment distribution, or an ion image. Reconstructing the sphere and measuring its radius gives the speed and therefore kinetic energy of the fragments in the bound molecule’s center-of-mass frame of reference. As an improvement over “standard” ion imaging, VMI involves focusing the newly formed
fragments with a series of ion optics; the voltages on the ion optics are tuned to minimize the impact of a parent molecule’s position upon photodissociation on the hit location of the formed fragments at the detector, significantly improving image resolution. VMI has been employed in experiments using reactive/non-reactive collisions\textsuperscript{13} or light\textsuperscript{14} to induce fragmentation. Coupling laser photolysis to VMI, the fragment kinetic energy release (KER) of photodissociation of a parent ion species gives a precise bond energy regardless of whether the onset to photodissociation is thermodynamic or spectroscopic and works well when there is a low density of states near $D_0$. The most common imaging technique used to measure bond energies pairs VMI with REMPI (resonance-enhanced multiphoton ionization). With this combination, far more bond energies of neutral molecules have been measured than those of their ions, and of non-metal ions than metal-containing ions. To measure bond energies of an ion with REMPI, its neutral analog is ionized via absorption of two or more photons, then the ion is photodissociated by an additional photon. An alternative to the various REMPI schemes involves directly making the ion of interest in an ion source first, instead of the neutral analog, and imaging its dissociation products by photolysis with a single laser. This method gives bond energy measurements in agreement with, and with similar precision to, REMPI measurements, but with far higher ion signal (and thus much shorter image collection times). It also allows for mass-selection of the species of study prior to photolysis, enabling the use of source configurations that form a variety of molecular species. This latter approach, imaging direct dissociation, is employed in this work.

The home-built reflectron time-of-flight (TOF) velocity map imaging instrument\textsuperscript{15} used for the studies presented in the following chapters is dual-purpose, capable of
measuring gas-phase cations’ (1) photodissociation spectra in the ultraviolet and visible (UV-Vis) and (2) thermodynamics and dissociation dynamics. In this instrument, the ions of interest are formed directly in a laser ablation ion source and guided into a quadrupole ion trap where they are held to thermalize with a buffer gas injected prior to the ions’ arrival. The ions are then extracted and accelerated. Direct dissociation of the parent species is then probed spectroscopically by scanning a photolysis laser, or images of the photofragments are collected at selected photolysis wavelengths. Image KER is subtracted from the photolysis energy which, by conservation of energy and momentum, gives a measurement of the parent ion’s bond dissociation energy. In images showing multiple fragmentation pathways, the energies and spacing of the corresponding multiple KER peaks reveal the product quantum states and the relative peak intensities reflect the branching ratio between different channels. This informs on dynamics far from the Franck-Condon region of the potential energy diagram. In addition, anisotropy in the image indicates whether the transition involved is parallel (Δλ=0) or perpendicular (Δλ=±1), and how much faster than the molecule’s rotational period subsequent dissociation occurs. When complemented with photodissociation spectra, imaging informs on the nature of the excited state(s) accessed in the transition, and which other states they may couple to in the dissociation process as a function of available energy.

This work reports the studies of several MX⁺ species by a combination of photofragment velocity map imaging, spectroscopy, and theoretical calculations to expand the library of detailed fundamental data on metal ion – ligand bonding. In chapter 2, the bonding, thermodynamics, and dissociation dynamics of NiO⁺ and NiS⁺ are determined, and the resulting observed differences are discussed. In chapter 3, one- and two-photon
fragmentation pathways of the MgI\(^+\) molecule are probed in the visible and UV. On the surface, each of these molecules appears well-suited to study by photodissociation spectroscopy, as none are predicted to absorb strongly enough near D\(_0\) to be dominated by fluorescence rather than photodissociation. This work shows that, while fluorescence near D\(_0\) is likely minimal for these systems, other factors make it difficult to determine parameters of interest one can usually obtain from photodissociation spectra. These factors and the systems they are illustrated in can be summarized as (1) insufficient absorption near D\(_0\) to obtain any spectroscopic information (NiO\(^+\)); (2) moderate absorption near D\(_0\) leading to a complex photodissociation spectrum (NiS\(^+\)); and (3) strong absorption near an excited product state threshold leading to preference for resonance enhanced photodissociation (MgI\(^+\)). Although in each of these cases photodissociation spectroscopy provided small clues, imaging the photofragments was key to determining the thermodynamics and dissociation mechanism. The main takeaway here is that information can be gained by photofragment imaging any molecular ion, regardless of how well-suited it is to study by photodissociation spectroscopy.

1.5 Experimental Methods

Experimental studies of NiO\(^+\), NiS\(^+\) and MgI\(^+\) were carried out on a home-built photofragment ion imaging instrument.\textsuperscript{15} This section provides an overview of the instrument and a description of the experiments. Nickel oxide and nickel sulfide cations are formed by laser ablating (2\textsuperscript{nd} harmonic of a Continuum Minilite II Nd:YAG laser) a rotating nickel disk in the presence of a gas mixture of either 10\% O\(_2\) in He (for NiO\(^+\)) or 0.5\% CH\(_3\)SH in He (for NiS\(^+\)), introduced via a pulsed valve (Parker Series 9). Magnesium
iodide cations are formed by ablating a magnesium disk in the presence of a gas mixture of CH₃I in He. The CH₃I/He mix is formed by flowing He over a reservoir of CH₃I (l) (Alfa Aesar, 99%, stabilized with copper) before entering the pulsed valve.

Ions are then directed through a linear quadrupole ion guide into a refrigerated radiofrequency 3D quadrupole ion trap. A pulse of He or D₂ buffer gas is injected to help thermalize the ions to the trap temperature. After thermalizing with the buffer gas for ~55 ms, ions undergo Wiley-McLaren extraction and are accelerated to a kinetic energy of 1800 V; after acceleration, the ions are re-referenced to ground potential. Ions are then mass selected by pulsing the voltage on a set of deflectors and are guided by a second set of deflectors into a reflectron.

For measuring photodissociation spectra, the ion beam interacts with the output of a pulsed dye laser (Continuum ND6000, 0.1 cm⁻¹ linewidth); the dye laser is pumped by the second (532 nm) or third (355 nm) harmonic of a Nd:YAG laser (Continuum Powerlite 8020). The laser beam intersects the ion beam at the ions’ turning point in the reflectron. The parent and resulting fragment signals are monitored with a microchannel plate (MCP) detector while scanning the dye laser wavelength.

For photofragment imaging, the reflectron is grounded and the deflector voltages are tuned in order to direct the ion beam through an adjustable iris positioned after the reflectron. After passing through the iris, the beam enters a series of velocity map imaging (VMI) optics. The parent ions are photolyzed between the first and second ion optic plates by the pulsed dye laser. Voltages on the first and second VMI optics are pulsed simultaneously with the laser to focus the newly formed fragment ions onto an imaging detector (coupled MCP-Phosphor screen, Photonis). In order to separate the two species in
time, the fragment and remaining parent ions are accelerated between the second and third VMI optics. The imaging detector then receives a high voltage pulse sufficiently wide to capture all of the fragment ion signal and discriminate against the parent ions. Photofragment images are collected by a CCD camera facing the phosphor screen for ~20,000 to 100,000 laser shots. Images were measured with the ion trap at 55 K and He buffer gas for NiO\(^+\), at 80 K with D\(_2\) buffer gas for NiS\(^+\) and at 200 K with He buffer gas for MgI\(^+\). Images are compiled with the NuACQ data acquisition software\(^{16}\) and image analysis (fragment cloud reconstruction and kinetic energy analysis) is performed using the BASEX method.\(^{17}\) The image anisotropy parameter (\(\beta\)) is determined using the Polar Onion-Peeling (POP) method.\(^{18}\)
CHAPTER 2
THE NICKEL OXIDE AND NICKEL SULFIDE CATIONS

2.1 Introduction

Several gas phase transition metal oxide cations (MO+) activate methane and convert it to methanol at room temperature.\textsuperscript{5,19–26} The most effective species for this reaction is NiO+, converting methane to methanol with over 99% selectivity and 20% efficiency.\textsuperscript{20,23} Transition metal sulfide cations (MS+) do not activate methane\textsuperscript{27} but do activate C-H bonds in larger hydrocarbons (as do most MO+). For example, NiS+ reacts with ethane to form a variety of neutral products, including ethene (51%), ethane thiol (11%) and H\textsubscript{2}S (38%), while NiO+ reacts to form only water and NiC\textsubscript{2}H\textsubscript{4}+.\textsuperscript{20,27} While experimental work has revealed important information about C-C and C-H bond activation by metal-containing ions (MX+), it remains difficult to predict and model these reactions. MX+ are very challenging molecules to treat theoretically, as they tend to have many unpaired electrons, numerous low-lying electronic states, and often can’t be well described by a single electronic configuration. Ideally, efficient methods, such as Density Functional Theory (DFT) could be used to characterize these molecules, but the lack of accurate and precise experimental thermodynamic information on a wide variety of metal-containing molecules makes it hard to assess the accuracy of different functionals and approaches. Even fundamental properties like M+X bond dissociation energies ($D_0$) are often not known to useful precision, leaving large uncertainty in reaction thermodynamics and mechanistic feasibility.
There have been some experimental and theoretical studies of NiO$^+$ and NiS$^+$. Calculations, first by Nakao et al.$^{28}$ at the B3LYP and high-level multi-reference configuration interaction (MRCI) level, and more extensive MRCI calculations by Sakellaris and Mavridis$^{29}$ unambiguously determined that the ground electronic state of NiO$^+$ is the $^4\Sigma^-$ state. The lowest-lying excited state was found to be the $^1\Delta$, lying $\approx$67 kJ/mol above the ground state.$^{29}$ These two states are also the two lowest lying in the isoelectronic NiS$^+$ molecule, but they are shifted significantly in energy relative to one another. B3LYP$^{30}$ and CCSD(T)$^{31}$ calculations predict that the ground state of NiS$^+$ is the $^1\Delta$ state, lying only $\approx$2-3 kJ/mol below the $^1\Sigma^-$ state. The two states are so close in energy that the calculations do not determine the ground state. The few experimental studies of NiO$^+$ and NiS$^+$ suggest the oxide is more strongly bound. Armentrout and co-workers report$^{32}$ $D_0$(NiO$^+$) = 260.7 ± 6.6 kJ/mol or more recently,$^{33}$ 254 ± 19 kJ/mol. The same group measured $D_0$(NiS$^+$) = 237 ± 4 kJ/mol,$^{34}$ which agrees with a previous estimate of an upper limit by our group ($D_0$(NiS$^+$) ≤ 238 ± 4 kJ/mol).$^{30}$ Theoretical values of $D_0$(NiO$^+$)$^{28,29,35}$ and $D_0$(NiS$^+$)$^{30,31}$ are all systematically lower than these experimentally measured values. It is worth noting the suggested trend in oxide$^{14,32,33,36-42}$ and sulfide$^{34,43-46}$ $D_0$ values for Ni$^+$ is identical to that for Sc$^+$, Ti$^+$, V$^+$, Cr$^+$ Mn$^+$, Fe$^+$ and Co$^+$, but opposite Cu$^+$ and Zn$^+$. While the photodissociation spectrum of NiO$^+$ has not previously been measured, Hettich et al.$^{47}$ recorded the spectrum of NiS$^+$ from 230 to 480 nm using an arc lamp and monochromator with 10 nm resolution. More recently, our group$^{30}$ used a dye laser with 0.1 cm$^{-1}$ linewidth to measure the spectrum from 20000 to 23000 cm$^{-1}$. The NiS$^+$ spectrum features a vibrational progression with 12 major peaks, each containing underlying spin-orbit structure. The reported$^{30}$ value of $D_0$(NiS$^+$) ≤ 238 ± 4 kJ/mol is based
on the observed fragmentation onset; uncertainty in the measurement considers the possibility that the observed onset results from photodissociation of hot ions.

Further experimental studies on the electronic structure and dynamics of NiO$^+$ and NiS$^+$ are needed to bolster theory and to better understand chemical bonding and thermodynamics in these systems. Photofragment velocity map imaging (VMI) has proven to be a useful experimental tool for measuring precise bond dissociation energies and dissociation dynamics in small molecules\textsuperscript{11,12,48–51} and ions.\textsuperscript{15,41,52–57} When complemented with spectroscopic measurements and theory, VMI gives an informative picture of how a photoexcited molecule moves around its potential energy surfaces. In this study, we probe the electronic structure, thermodynamics and photodissociation dynamics of NiO$^+$ and NiS$^+$ with a combination of theory, photofragment spectroscopy and ion velocity map imaging.

### 2.2 Theoretical Methods

Calculations of the ground and several excited electronic states of NiO$^+$ and NiS$^+$ were carried out at the MRCI level using the MOLPRO\textsuperscript{58,59} software package. For NiO$^+$ these calculations are very similar to those of Sakellaris and Mavridis,\textsuperscript{29} but included additional excited electronic states at higher energies, relevant to the experimental spectra. The MRCI calculations consist of a complete active space self-consistent field (CASSCF) calculation followed by single and double excitations from the active space. The CASSCF active space consists of the 4s and 3d orbitals on nickel and 2p on oxygen (13 electrons in 9 orbitals), and 12 quartet states of each symmetry are state averaged, with equal weights. For the MRCI, the active space is expanded to also allow promotions from the 2s orbital
on oxygen, as was done by Sakellaris and Mavridis. The default, internally contracted (icMRCI) method was used. All calculations are carried out in $C_2v$ symmetry, and states of each symmetry are calculated separately. The calculations use the aug-cc-pVQZ basis set for all atoms and include the Davidson correction, so they are at the MRCI+Q/aug-cc-pVQZ level.

For NiS$^+$, some potential energy curves using this active space do not dissociate to the correct, ground state products. This is a well-known\textsuperscript{60,61} problem with CASSCF calculations involving the late transition metals, and is due to there being more possible states (and hence more correlation) arising from $d^{n-1}s^1$ configurations than $d^n$. For Ni$^+$, this favors formation of the 3$d^8$ 4$s$ ($^4$F) first excited state rather than the 3$d^9$ ($^2$D) ground state. The solution is to add additional d orbitals on the metal (typically called the d’ space) to the active space, and in this case a complete set of five d orbitals was required. The CASSCF active space then consists of 13 electrons in 14 orbitals. For each symmetry, all quartet states correlating to Ni$^+$ ($^4$F) and Ni$^+$ ($^2$D) + S ($^3$P) were averaged. This corresponds to three $\Sigma^+$, five $\Delta$ and one $\Gamma$ state (a$_1$ symmetry); six $\Pi$ and three $\Phi$ states (b$_1$ or b$_2$); and three $\Sigma^-$, five $\Delta$ and one $\Gamma$ state (a$_2$ symmetry). The resulting CASSCF potentials then dissociate to the correct asymptotes. For the MRCI, the active space is expanded to also allow promotions from the 3$s$ orbitals on sulfur. In addition, 12 excited states are calculated to ensure that the 9 lowest states are included. Unfortunately, the larger CASSCF active space leads to a prohibitively large icMRCI calculation. In order to make the icMRCI calculation tractable, a subset of the configuration state functions (CSFs) with norm $>0.04$ were selected, typically leading to $\sim200$ CSFs and $\sim1.6 \times 10^7$ configurations in the icMRCI.
In order to assess whether there are low-lying doublet or sextet states, calculations on those states were also carried out at the MRCI+Q/aug-cc-pVQZ level. The lowest sextet state lies >10000 cm\(^{-1}\) above the lowest quartet states, so they were not considered further. The lowest doublet state is the \(^2\Pi\), which is predicted to lie \(\sim 1500\) cm\(^{-1}\) above the lowest quartet states. Spin-orbit calculations which simultaneously included the low energy \(^4\Sigma^+\), \(^4\Delta\) and \(^2\Pi\) states were also carried out (without the d’ space) using MOLPRO, using the MRCI wavefunctions and the Breit-Pauli spin-orbit operator for internal configurations and a mean-field one-electron Fock operator for external configurations.\(^{58,59}\)

2.3 Results and Discussion

2.3.1 NiO\(^+\)

2.3.1.1 Electronic Structure of NiO\(^+\)

The ground state of NiO\(^+\) was determined to be \(^4\Sigma^+\) by Nakao et al. in 2001\(^{28}\) using B3LYP and MRCI calculations. This was confirmed by a wider range of MRCI calculations performed by Sakellaris and Mavridis in 2013.\(^{29}\) Bond dissociation energy \((D_0)\) values calculated in these studies range from 19000 to 21000 cm\(^{-1}\), with the latter group reporting a recommended value of 19200 cm\(^{-1}\).\(^{29}\) Sakellaris and Mavridis also characterized a wide range of excited electronic states, of several spin multiplicities. There are nine electronic states (\(\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(2), \Phi\)) for each spin multiplicity (doublet and quartet), that correlate to Ni\(^+\) (\(^2\)D) + O (\(^3\)P) ground state products. They calculated seven of these states, for each spin. Excited Ni\(^+\) (\(^4\)F) + O (\(^3\)P) give rise to twelve states (\(\Sigma^+(2), \Sigma^-\), \(\Pi(3), \Delta(3), \Phi(2), \Gamma\)), each of which can have doublet, quartet or sextet spin. Of these,
they calculated a doublet, a quartet and four sextet predissociative states and 8 repulsive states. Our calculations focus on the quartet states and include all the states that correlate to Ni\(^+\) (\(^2\)D, \(^4\)F) + O (\(^3\)P). These are the most relevant states for optical spectroscopy, but do not include some states that may contribute to the photodissociation dynamics (e.g. predissociation via intersystem crossing). Figure 2.1 shows calculated MRCI+Q potentials of the ground \(^4\Sigma^-\) state of NiO\(^+\), along with several excited \(^4\Sigma^-\) and \(^4\Pi\) states. These are states that are optically accessible and have vertical excitation energies below 40000 cm\(^{-1}\). The transition intensity from the \(X\ \ ^4\Sigma^-\) state to each of these states is predicted to be weak (\(f \leq 0.003\)).

2.3.1.2 Photodissociation Spectrum of NiO\(^+\)

The photodissociation spectrum of NiO\(^+\) (Figure 2.2) over the range of 20350 to 27000 cm\(^{-1}\) (492 to 370 nm) shows no obvious fragment onset and little to no structure, gradually increasing from zero to low and constant fragment yield from 20800 to 25000 cm\(^{-1}\). Since an onset to form ground state Ni\(^+\) products was not observed, measurements of the spectrum were extended to energies above the Ni\(^+\) (\(^4\)F) threshold in hope of detecting a significant increase in fragment yield which might mark the opening of the higher energy product channel. In this region of the spectrum (27000 to 29200 cm\(^{-1}\)), photofragment yield increases again starting at 27700 cm\(^{-1}\) with a small peak at 27800 cm\(^{-1}\), then continues to increase before it plateaus at 29000 cm\(^{-1}\) at approximately the same intensity as the peak at 27800 cm\(^{-1}\). The lack of a sharp onset in the spectrum near the predicted bond dissociation energy and again upon energetic access of a new product channel makes it difficult to precisely determine \(D_0\) (NiO\(^+\)) and characterize the excited states from the spectrum alone. However, imaging the photoproducts formed at different photon energies allows us to make
a precise $D_0$ measurement and gives us additional information on the dissociation dynamics.

2.3.1.3 Images of Ni$^+$ Fragments.

Figure 2.3 shows a photofragment image of Ni$^+$ from photodissociation of NiO$^+$ at 27778 cm$^{-1}$, along with the resulting total kinetic energy release (KER) distribution. There is moderate KER, indicating that only ground electronic state products are formed. The Ni$^+$ ground electronic state has two spin-orbit levels, with the $^2D_{3/2}$ lying 1507 cm$^{-1}$ above the $^2D_{5/2}$ ground state; for oxygen, the $^3P_1$ and $^3P_0$ are 158 and 227 cm$^{-1}$, respectively, above the $^3P_2$ ground state.$^{62}$ The KER is sufficiently high that the spin-orbit states are not resolved. However, the KER distribution shows that the propensity for $^2D_{3/2}$ products is higher than that for $^2D_{5/2}$ products. The distribution of signal intensity in the image is radially uniform (‘isotropic’). This case is the ‘midpoint’ in the continuum between two limiting cases of image anisotropy, captured by the anisotropy parameter ($\beta$). The first case, limiting parallel ($\beta = 2$), describes a direct photodissociation event where the transition dipole moment is oriented parallel to the principal molecular axis of the parent ion and photodissociation is prompt. If the photolysis laser is vertically polarized, this case gives an image with vertical anisotropy (higher signal intensity at the north and south poles). For a linear molecule, this occurs if the change in orbital angular momentum, $\Delta \Lambda$, is zero. The second case, limiting perpendicular ($\beta = -1$), describes a direct photodissociation event where the transition dipole moment is oriented perpendicular to the principal molecular axis. If the photolysis laser is vertically polarized, this gives an image with horizontal anisotropy (higher signal intensity at the equator). This occurs when $\Delta \Lambda = \pm 1$. The
'midpoint’ case, isotropic ($\beta = 0$), describes a photodissociation event where the parent ion is equally likely to fall apart in any orientation regardless of the laser polarization. This last case results in an image with no anisotropy and can occur if: (1) the excited molecules survive for several rotational periods before dissociating; or (2) at a given photolysis energy, the molecules photodissociate via multiple overlapping parallel and perpendicular transitions, whose contributions to the image anisotropy cancel each other out. For NiO$^+$ photolyzed at 27778 cm$^{-1}$, the calculations predict that both mechanisms are active. There are parallel transitions to the $2^4\Sigma^-$ and $3^4\Sigma^-$ states, both of which correlate to excited products and are thus predissociative at this energy. There is also a perpendicular transition to the $3^4\Pi$ state, which has a barrier to dissociation, due to an avoided crossing with the $4^4\Pi$ state.

Figure 2.4 (i) shows a Ni$^+$ photofragment image taken at slightly higher photon energy (29197 cm$^{-1}$) and its corresponding KER distribution. A new, low KER channel corresponding to dissociation to excited state Ni$^+$ ($^4F_J$) products clearly dominates over the ground state channel. The Ni$^+$ ($^4F_{9/2}$) state lies 8394 cm$^{-1}$ above the $^2D_{5/2}$ ground state, and the J = 7/2, 5/2 and 3/2 spin-orbit levels lie 936, 1722 and 2270 cm$^{-1}$ above the J = 9/2 level, respectively. Taking the $^4F_J$ energy splitting into account, the KER distribution in Fig. 2.4 (i) is, further, consistent with exclusive formation of the lowest energy spin-orbit component, Ni$^+$ ($^4F_{9/2}$). In contrast to the near isotropic image in Figure 2.3 ($\beta = 0.10$), the image in Figure 2.4 (i) shows slight parallel anisotropy ($\beta = 0.30$) suggesting photodissociation at 29197 cm$^{-1}$ is more prompt and is due to excitation to a $^4\Sigma^-$ state. Dissociation at progressively higher energies leads to production of the other $^4F_J$ spin-orbit states. While the kinematics of detecting the heavy Ni$^+$ fragment in dissociation of NiO$^+$
are not ideal for maximum resolution and O \(^3\)P\(_j\) spin-orbit states (227 cm\(^{-1}\) spread) ‘smear’
the Ni\(^+\) rings, we are still able to resolve the lowest two spin orbit states (936 cm\(^{-1}\) spacing)
of the Ni\(^+\) \(4F\)\(_j\) fragments at a photolysis energy of 30075 cm\(^{-1}\) (Figure 2.5). Ni\(^+\) \(4F_{9/2}\)
fragments account for \(~80\%\) of the photoproduct yield, with Ni\(^+\) \(4F_{7/2}\) making up the
remaining 20\%. At 30769 cm\(^{-1}\) however, with Ni\(^+\) \(4F_{5/2}\) becoming energetically
accessible, individual Ni\(^+\) spin orbit levels are less well resolved (Figure 2.4, ii). Although
the Ni\(^+\) \(4F_{3/2}\) product channel is energetically accessible by 31646 cm\(^{-1}\), it is highly
unfavored relative to each of the lower energy spin-orbit channels (Figure 2.4, iii). It is
apparent from the KER distributions in Figure 2.4 (ii, iii) that the propensity for Ni\(^+\) \(4F\)\(_j\)
spin-orbit state products generally decreases as the energy of the spin orbit state increases.
The trend in spin-orbit propensities for Ni\(^+\) \(4F\)\(_j\) products is opposite that for \(^2\)D\(_j\) products.
In addition, parallel anisotropy is consistent across all images (Fig. 3, \(\beta = 0.30\), inner ring
and 1.06, outer ring; Fig. 2.4 ii) \(\beta = 0.31\), inner ring and 1.14, outer ring; Fig. 2.4 iii) \(\beta =
1.65\) collected at photolysis energies above the Ni\(^+\) \(4F\) product threshold, suggesting
dissociation over this entire region results from excitation to the same or other nearby
\(^4\Sigma^-\) state(s). Based on the calculations, this is likely the \(^3\)\(^4\Sigma^-\) state, which has a significantly
larger bond length than the ground state, so vertical excitation accesses the repulsive inner
wall of the potential.

For a given image, subtracting the peak total KER in the KER distribution from the
photolysis energy gives a precise value of the product threshold, and upon subtraction of
the Ni\(^+\) \(4F\) product energy, the NiO\(^+\) bond dissociation energy \((D_0)\). A more accurate
approach is to plot photolysis energy (with excited photoproduct energy subtracted) versus
total KER for a series of images above the Ni\(^+\) \(4F\) threshold and fit the points to a line.\(^{63}\)
The y-intercept of the plot is equal to $D_0$, as shown in Figure 2.6. This intercept method gives the most precise measurement of the NiO$^+$ bond dissociation energy reported to date ($D_0 = 244.6 \pm 2.4 \text{ kJ/mol}, \ 20450 \pm 200 \text{ cm}^{-1}$). Table 2.1 compiles all experimentally measured values and selected theoretical values of $D_0$ (NiO$^+$). Our VMI measured $D_0$ agrees with the later, less precise guided ion beam measurement by Armentrout and coworkers, but not with their earlier, more precise measurement. The most sophisticated ab initio calculations, at the MRCI level and with scalar relativistic effects using the second-order Douglas-Kroll-Hess (DKH2) approximation, are very close to our measured value, as is the averaged coupled pair functional (ACPF) result. Near the measured $D_0$, the photodissociation spectrum shows zero fragment yield, suggesting NiO$^+$ does not absorb at $D_0$, or that the fluorescence lifetime is shorter than the photodissociation lifetime. Lack of absorption at this photon energy is consistent with calculations by Sakellaris and Mavridis, which predict the two closest excited states to the Ni$^+$ ($^3D_J$) product threshold to be the $^4\Gamma$ ($T_e = 15504 \text{ cm}^{-1}$) and $^6\Delta$ ($T_e = 22107 \text{ cm}^{-1}$) states, neither to which are optically allowed transitions from the $^4\Sigma^-$ ground state, and our calculations, which predict that there are few excited states with allowed electronic transitions near the dissociation threshold, and transitions to those states are weak.

2.3.2 NiS$^+$

2.3.2.1 Electronic Structure of NiS$^+$

Although NiS$^+$ and NiO$^+$ are isoelectronic, the relative energies of their electronic states are quite different. The $^4\Delta$ state, which lies $\sim 6000 \text{ cm}^{-1}$ above the $^4\Sigma^-$ ground state in NiO$^+$, is predicted to be the ground state in NiS$^+$ with the $^4\Sigma^-$ lying only $\sim 200 \text{ cm}^{-1}$ higher
in energy at the B3LYP\textsuperscript{30} and CCSD(T)\textsuperscript{31} level. Our calculations, at the MRCI+Q/aug-cc-pVQZ level, predict that the $^4\Delta$ lies 627 cm\textsuperscript{-1} above the $^4\Sigma^-$. Figure 2.7 shows the potentials for all quartet states of NiS\textsuperscript{+} that correlate to Ni\textsuperscript{+} ($^2$D, $^4$F) + S. In this figure, $^4\Sigma^-$ and $^4\Delta$ states are highlighted, as they are accessible by parallel transitions from the $^1\Sigma^-$ and $^1\Delta$ states. Table 2.2 gives spectroscopic parameters for all of these states, while Figures 2.8 and 2.9 show selected excited states.

Spin-orbit coupling will preferentially stabilize the lowest lying spin-orbit levels of the $^4\Delta$ state relative to the $^4\Sigma^-$ state. In order to quantify this effect, we carried out spin-orbit calculations, including the three lowest-lying electronic states: the $^4\Delta$, $^4\Sigma^-$ and $^2\Pi$ states. These calculations were done using the standard (not expanded) d space for Ni, as including the d’ space in the spin-orbit calculations is prohibitively expensive. Also, the inclusion of the d’ space has only a small effect on the potentials near equilibrium. The results are shown in Figure 2.10. With this active space, the ground state is $^4\Sigma^-$, with the $^4\Delta$ and $^2\Pi$ states 403 and 838 cm\textsuperscript{-1} higher in energy, respectively. Including spin-orbit splitting, the ground state is $^4\Delta_{7/2}$. The $^4\Delta\Omega$ ($\Omega = 5/2, 3/2, 1/2$) states are at 454, 846, and 1655 cm\textsuperscript{-1}, respectively. To first order, $\Sigma$ states do not have spin-orbit splitting, but they can have second-order spin orbit splitting, which is typically much smaller. The $^4\Sigma^-_{3/2}$ state is at 26 cm\textsuperscript{-1} and the $^4\Sigma^-_{1/2}$ is at 66 cm\textsuperscript{-1}; the $^2\Pi_{3/2}$ is at 724 cm\textsuperscript{-1} and the $^2\Pi_{1/2}$ is at 1542 cm\textsuperscript{-1}. So, including spin-orbit interactions stabilizes the $^4\Delta_{7/2}$ and $^2\Pi_{3/2}$ states by 429 and 140 cm\textsuperscript{-1}, respectively, relative to the $^4\Sigma^-_{3/2}$ state. Combining this shift with the energies calculated using the expanded d space, the calculations predict that the $^4\Sigma^-_{3/2}$ is the ground state, only 198 cm\textsuperscript{-1} below the $^4\Delta_{7/2}$. This difference is smaller than the relative accuracy of
the calculations, which thus do not clearly indicate whether $^4\Delta$ or the $^4\Sigma^-$ is the true ground state. So, in the subsequent discussion we will consider optically allowed transitions from the $^4\Delta_{7/2}$, $^4\Sigma_{3/2}$ and $^4\Sigma_{1/2}$ states, as they may be populated at the temperature of the ion trap.

2.3.2.2 Photodissociation Spectrum of NiS$^+$

The photofragment spectrum of NiS$^+$ was measured by our group previously on a separate instrument, with ions formed by laser ablation and cooled by supersonic expansion. In this work, a segment of the spectrum was re-measured with ions cooled in a 3D quadrupole trap at several trap temperatures with He or D$_2$ buffer gas. No dissociation is observed below ~20000 cm$^{-1}$ and the spectra contain several peaks, with rich substructure (Figure 2.11). A few peaks change in intensity as the trap is cooled. One example is the lowest energy peak in the spectrum (labeled 1*, at 20022 cm$^{-1}$), which loses approximately half its intensity as the trap is cooled from 291 (red) to 80 K (blue). The reduced intensity suggests this peak arises from photodissociation of parent ions that are vibrationally excited or in a low-lying excited electronic or spin-orbit state rather than the ground state. Another example is the peak at 20164 cm$^{-1}$ (labeled 3), which increases in intensity by approximately two-fold from 291 K to 80 K. The gain in intensity suggests that peak 3 originates from the ground state of NiS$^+$. Although most of the remaining peaks in the spectrum become narrower and sharper as the trap is cooled, they do not change significantly in intensity.
2.3.2.3 Images of Ni$^+$ Fragments

Photofragment images were taken at several peaks in the spectrum to determine $D_0$ (NiS$^+$) and to determine the origin of the three lowest energy peaks in the spectrum (1, 2 and 3). The ground state of sulfur is $^3P_2$, with the $^3P_1$ and $^3P_0$ states at 396 and 574 cm$^{-1}$, respectively. The larger spin-orbit splitting of sulfur relative to oxygen and improved kinematics of NiS$^+$ relative to NiO$^+$ mean that the spin-orbit states of both fragments can be resolved near threshold. Figure 2.12 shows a photofragment image at 20631 cm$^{-1}$ (peak 4 in Figure 2.11). The resulting KER distribution has two distinct peaks spaced by ~400 cm$^{-1}$, consistent with formation of ground state Ni$^+$ ($^2D_{5/2}$) and both ground state S ($^3P_2$) (higher KER) and first excited spin-orbit state S ($^3P_1$) (lower KER) products. Both the lower and higher KER channels have slightly parallel fragment distribution ($\beta = 0.29$ and 0.28, respectively). This distribution is consistent with a parallel electronic transition where dissociation to S ($^3P_1$) products competes with dissociation to the S ($^3P_2$) channel, with a product branching ratio of 3:2. At 21706 cm$^{-1}$ (peak 5 in Figure 2.11), Ni$^+$ ($^2D_{5/2}$) + S ($^3P_{0,1,2}$) products are all formed (70%) and compete with Ni$^+$ ($^2D_{3/2}$) + S ($^3P_2$) (30%) as shown in Figure 2.13. The higher KER channel corresponding to Ni$^+$ ($^2D_{5/2}$) has slight parallel anisotropy ($\beta = 0.43$), while the lower KER channel is isotropic ($\beta = 0.08$).

A photofragment image at 20164 cm$^{-1}$ (peak 3) shows only formation of Ni$^+$ ($^2D_{5/2}$) + S ($^3P_2$), with low KER, and gives a dissociation energy that is consistent with those from the higher-energy peaks. However, images at 20022 and 20103 cm$^{-1}$ (peaks 1* and 2*) give significantly lower $D_0$, indicating that they arise from hot ions. Based on the KER distributions, and assuming ground state products, peaks 1* and 2* are due to ions with an internal energy of 166 ± 50 cm$^{-1}$ and 81 ± 30 cm$^{-1}$, respectively. We therefore assign peaks
including and to the blue of peak 3 as originating from ground state \((1^4 \Delta \text{ or } 1^4 \Sigma^{-})\) NiS\(^{+}\). The fundamental vibrational frequencies of the \(1^4 \Delta\) and \(1^4 \Sigma^{-}\) states are calculated to be \(v_0 = 417\) and \(413\) cm\(^{-1}\), respectively (Table 2.2), so peaks 1\(^{*}\) and 2\(^{*}\) are not due to vibrational hot bands. Rather, peaks 1\(^{*}\) and 2\(^{*}\) likely originate from higher lying spin-orbit levels of the low-lying \(4 \Delta\) and \(4 \Sigma^{-}\) states. As argued below, we assign the ground level as \(4 \Delta_{7/2}\) and the hot bands as originating from the \(4 \Sigma_{3/2}\) and \(4 \Sigma_{1/2}\) levels.

The dissociation energy of NiS\(^{+}\) is determined by plotting photolysis energy versus total KER for production of ground state products determined at several photolysis energies and fitting the points to a line. The results, shown in Figure 2.14, give \(D_0 (\text{NiS}^{+}) = 240.3 \pm 1.4\) kJ/mol, \(20090 \pm 120\) cm\(^{-1}\). Experimentally measured and selected theoretical values of \(D_0 (\text{NiS}^{+})\) are shown in Table 2.3. Rue et al.\(^{34}\) measured the bond strength using the endothermic reaction of Ni\(^{+}\) with OCS in a guided ion beam instrument. Hettich et al.\(^{47}\) measured the photodissociation of NiS\(^{+}\) in an ICR, using a lamp/monochromator with 10 nm resolution, and assuming that the dissociation onset occurs at the bond dissociation energy. Our previous study,\(^{30}\) using laser photodissociation, determined the onset with much higher precision but was still limited by uncertainty in whether small peaks near the dissociation onset are due to hot ions. Our VMI measurement of \(D_0 (\text{NiS}^{+})\) agrees with all of the previous values but has higher precision. Calculations by Lakunza et al.\(^{31}\) at the CCSD(T)/TZVP++G(3df,2p)//B3LYP level \((D_0 (\text{NiS}^{+}) = 234\) kJ/mol) and, in this work, at the MRCI+Q/aug-cc-pVQZ level (235 kJ/mol) are nearly identical and quite close to the measured value, underestimating the bond strength by 5-6 kJ/mol. The present study confirms that dissociation occurs at the thermodynamic onset, and determines that the first two, small, peaks in the spectrum are from hot ions. Thus, even when dissociation occurs
at the thermodynamic onset, imaging is a valuable complement to spectroscopy. Our measurement of $D_0$ (NiS$^+$) also refines the ionization energy of NiS. Matthew et al.$^{64}$ recently measured the dissociation energy of the neutral with very high precision: $D_0$ (NiS) = 3.651 ± 0.003 eV. Combining this value with our measurement of $D_0$ (NiS$^+$) and IE (Ni), we obtain a more precise estimate of IE (NiS) = 8.80 ± 0.02 eV (849 ± 1.7 kJ/mol).

The MRCI+Q calculations, in conjunction with the images, help to assign the photodissociation spectrum. The fragment anisotropy in the images ranges from parallel to isotropic. Also, as shown in Table 2.2, the calculated oscillator strengths for perpendicular transitions are much smaller than for parallel transitions. Thus, we assign the majority of the spectrum to be due to parallel transitions, $4\Sigma^+ \leftarrow 4\Sigma^-$ or $4\Delta \leftarrow 4\Delta$. The only $4\Sigma^-$ state in the relevant energy region is the $3 \ 4\Sigma^-$ state, shown in blue, bold in Figure 2.7. This state has calculated $T_0 = 19006 \text{ cm}^{-1}$, a vertical transition energy of $21382 \text{ cm}^{-1}$, a vibrational frequency of $\omega_e = 314 \text{ cm}^{-1}$, and integrated oscillator strength of $f = 0.0103$. Experimentally, the dissociation yield for NiS$^+$ is significantly higher than for NiO$^+$ and is consistent with an integrated oscillator strength of this magnitude. A simulated absorption spectrum due to this transition ($3 \ 4\Sigma^- \leftarrow 1 \ 4\Sigma^-$) is shown in the dashed blue trace at the bottom of Figure 2.11. This simulated spectrum is far less complex than is experimentally observed. If second-order spin-orbit splitting is included, the propensity is for $4\Sigma^{-3/2} \leftarrow 4\Sigma^{-3/2}$ and $4\Sigma^{-1/2} \leftarrow 4\Sigma^{-1/2}$ transitions rather than $4\Sigma^{-1/2} \leftarrow 4\Sigma^{-3/2}$ and $4\Sigma^{-3/2} \leftarrow 4\Sigma^{-1/2}$. This would lead to a series of doublets whose relative intensities would depend on the temperature of the ion trap, which is not observed in the experiment, so it is unlikely that the observed spectrum is solely due to transitions from a $4\Sigma^-$ state. There are three $4\Delta$ states in the energy region of interest, the 3, 4 and 5 $4\Delta$, shown in green, bold in Figure 2.7. These
states have several avoided crossings at energies near 20000 cm\(^{-1}\) and the resulting potentials are anharmonic. Transitions to all three from the \(1^4\Delta\) are predicted to be fairly intense, with \(f = 0.0088\) for \(3^4\Delta\) and 0.0132 and 0.0079 for the 4 and 5 \(4\Delta\). The simulated spectra, shown in the green dashed traces at the bottom of Figure 2.11, are quite complex, as they contain contributions from all three states at low energy, and then simplify somewhat above \(~21500\) cm\(^{-1}\) when contributions from the 4 and 5 \(4\Delta\) dominate. Simulated spectra due to the \(3^4\Sigma^- \leftrightarrow 1^4\Sigma^-\) and \(3, 4, 5^4\Delta \leftrightarrow 1^4\Delta\) transitions were summed to give the total simulated spectrum, shown in the red dashed trace at the bottom of Figure 2.11. Intensities in the total spectrum were multiplied by 3 for easier visualization. Some (but not all) of the multiplet structure in the first five features of the experimental spectrum (20000 – 21200 cm\(^{-1}\)) is captured by the simulation, with triplets or doublets (depending on the simulated Gaussian width) predicted to arise from the \(3^4\Sigma^- \leftrightarrow 1^4\Sigma^-\) and \(4, 5^4\Delta \leftrightarrow 1^4\Delta\) transitions. The remaining seven features in the experimental spectrum are clear doublets, a motif which is well-modeled by the simulation, which indicates they are due to transitions to the 4 and 5 \(4\Delta\) states. The relative intensities of peaks in the simulated doublet and triplet features do not precisely match experimental intensities. However, the three \(4\Delta\) states all lie at similar energies and interact, making it challenging to accurately calculate their relative intensities and energies. We therefore assign the bulk of the spectrum to \(4^4\Delta \leftrightarrow 1^4\Delta\) and \(5^4\Delta \leftrightarrow 1^4\Delta\) vibronic transitions, with perhaps some contribution from the \(3^4\Sigma^- \leftrightarrow 1^4\Sigma^-\) transition below 20700 cm\(^{-1}\). We also assign hot band peaks 1* and 2* to transitions to the \(3^4\Sigma^-\) state from the \(1^4\Sigma_{1/2}^-\) and \(1^4\Sigma_{3/2}^-\) states, respectively, based on varied temperature spectra and KER distributions of images taken at the corresponding
photon energies. This implies that the $1^4\Sigma_{1/2}^-$ and $1^4\Sigma_{3/2}^-$ states lie $166 \pm 50$ and $81 \pm 30 \text{ cm}^{-1}$ respectively above the $1^4\Delta_{7/2}$ ground state.

It is useful to compare the electronic states of NiS$^+$ with isoelectronic CoS, which has been studied more extensively by experiment and theory. Although an early atom superposition and electron delocalization molecular orbital (ASED-MO) theory calculation$^{65}$ on CoS assumed a $^4\Sigma^-$ ground state, subsequent studies by Bauschlicher and Maitre$^{66}$ at the CCSD(T) and ACPF level correctly predict a $^4\Delta$ ground state, and a DFT study by Bridgeman and Rothery$^{67}$ predicts that the $^4\Sigma^-$ lies $1770 \text{ cm}^{-1}$ above the $^4\Delta$. Ziurys and coworkers$^{68}$ measured the microwave spectrum of CoS and determined the ground state to be $^4\Delta_{7/2}$, with $r_0 = 1.97798506 \text{ Å}$. An infrared emission study by Bernath and coworkers characterized the low-lying $^4\Phi (T_0 = 3409 \text{ cm}^{-1})$ and $^4\Pi (T_0 = 5620 \text{ cm}^{-1})$ states.$^{69}$ As part of a series of studies$^{70–72}$ on CoS, Chen and coworkers measured the laser-induced fluorescence spectrum$^{70}$ of jet-cooled CoS from 15200 to 19000 $\text{ cm}^{-1}$. They observed 57 vibronic bands and assigned them to five different electronic transitions. Four of these are transitions to different $^4\Delta_{7/2}$ states and one is a transition to a $^4\Pi_{3/2}$, all from the $^4\Delta_{7/2}$ ground state. This analysis of the CoS LIF spectrum from 15200 to 19000 $\text{ cm}^{-1}$ echoes our assignment of three separate $^4\Delta \leftarrow 1^4\Delta$ transitions in the NiS$^+$ photodissociation spectrum from 19900 to 23200 $\text{ cm}^{-1}$.

2.3.3 Comparison of Bonding in MO$^+$ and MS$^+$

Figure 2.15 and Table 2.4 compare the M$^+$-O and M$^+$-S bond strengths for the 3d transition metals. The early transition metal cations form extremely strong bonds to oxygen, and much weaker bonds to sulfur. The late transition metals form much weaker
bonds to oxygen, and, for each metal, the $M^+-O$ and $M^+-S$ bond dissociation energies are similar. This trend in bonding, and its dependence on the occupied molecular orbitals has been discussed in detail for the cations,\textsuperscript{29,46,73,74} and neutrals\textsuperscript{66,67,75} and will be reviewed here. For some molecules, there is substantial multi-configurational character, so this description is only approximate. The valence molecular orbitals of the transition metal oxides and sulfides primarily arise from the 3d and 4s orbitals on the metal and the oxygen 2s and 2p, or sulfur 3s and 3p. These lead to four $\sigma$, two pairs of $\pi$ and one pair of $\delta$ molecular orbitals. The orbitals for NiO$^+$ and NiS$^+$ are shown in Figure 2.16. These orbitals will first be described for MO$^+$, then similarities and differences between the oxides and sulfides will be discussed. The non-bonding $1\sigma$ is almost entirely 2s on oxygen. The $2\sigma$ is a bonding combination of 3d$\sigma$ (3d$_{z^2}$) on the metal and 2p$_z$ on oxygen. The $1\pi_x$ and $1\pi_y$ are bonding combinations of metal 3d$\pi$ (3d$_{xz}$ and 3d$_{yz}$) and oxygen 2p$_x$ and 2p$_y$. For ScO$^+$ there are 8 valence electrons, so these four orbitals are filled, leading to a strong Sc$^+$-O bond. In TiO$^+$ and VO$^+$ the additional electrons populate the non-bonding 1$\delta$+ and 1$\delta$- orbitals and are unpaired. These orbitals are the metal 3d$\delta$ (3d$_{xy}$ and 3d$_{x^2-y^2}$). For CrO$^+$ and MnO$^+$, rather than add electrons to the 1$\delta$ to form low-spin states, they are unpaired and go into the anti-bonding 3$\sigma$ and 2$\pi$ orbitals, respectively.\textsuperscript{74} As a result, the Cr$^+$-O bond is significantly weaker than in the earlier metals, and the Mn$^+$-O bond is weaker still. High spin is again favored for FeO$^+$, whose $^6\Sigma^+$ ground state has unpaired electrons in the 1$\delta$+, 1$\delta$-, 2$\pi_x$, 2$\pi_y$ and 3$\sigma$. In CoO$^+$ and NiO$^+$ the additional electrons go into the 1$\delta$ orbitals, so FeO$^+$, CoO$^+$ and NiO$^+$ have similar bond strengths. CuO$^+$ has a significantly weaker bond, as the 3$\sigma$ is now doubly occupied. In ZnO$^+$ the next electron goes into the 2$\pi$. The reduced covalency means that the bonding in CuX$^+$ and ZnX$^+$ ($X = O, S$) can be viewed as largely
electrostatic in nature, which leads to similar bond strengths for CuX$^+$ and ZnX$^+$, and for larger bond strengths for the sulfides than the oxides, due to the greater polarizability of sulfur.$^{46}$

Although the orbitals in MO$^+$ and MS$^+$ are similar, there are important differences. Compared to those in MO$^+$, the bonding orbitals in MS$^+$ have less bonding character and the antibonding orbitals have less antibonding character. The 1$\pi$ in MS$^+$ is less strongly bonding, which helps to explain why the M$^{+}$-S bond strengths are $\sim$200 kJ/mol lower than those of M$^{+}$-O for M=Sc, Ti, V. Concomitantly, the 2$\pi$ has much less electron density on the metal and is thus much less strongly antibonding. So, occupying the 2$\pi$ reduces the M$^{+}$-S bond strength, but to a much lesser extent than for the oxides. Also, the 3$\sigma$ in MS$^+$ is nearly completely metal 3$d_{xz}$ and is non-bonding, rather than anti-bonding. So, there is little reduction in the M$^{+}$-S bond strength as this orbital is occupied. This observation underlies a key difference between the electronic structures of NiO$^+$ and NiS$^+$. In NiS$^+$ calculations predict that the 4$\Sigma^-$ and 4$\Delta$ are nearly degenerate and have very similar bond lengths and vibrational frequencies. The dominant electron configuration for the 4$\Sigma^-$ state is 1$\sigma^2$ 2$\sigma^2$ 1$\pi_x^2$ 1$\pi_y^2$ 1$\delta_x^2$ 1$\delta_z^2$ 2$\pi_x^1$ 2$\pi_y^1$ 3$\sigma^1$ (MRCI coefficient of 0.82), while for the 4$\Delta$ state it is 1$\sigma^2$ 2$\sigma^2$ 1$\pi_x^2$ 1$\pi_y^2$ 1$\delta_x^2$ 1$\delta_z^2$ 1$\delta^1$ 2$\pi_x^1$ 2$\pi_y^1$ 3$\sigma^2$ (MRCI coefficient of 0.79). Thus, there is little difference in energetics or bonding between having an extra electron in the 1$\delta$ or 3$\sigma$ orbital. The situation is quite different for NiO$^+$. The ground state is clearly 4$\Sigma^-$, with the 4$\Delta$ state 5600 cm$^{-1}$ higher in energy at the MRCI+Q level.$^{29}$ In addition, the 4$\Delta$ state has a substantially longer bond (1.708 Å vs. 1.588 Å) and lower vibrational frequency than the 4$\Sigma^-$ state.$^{29}$ So, the 3$\sigma$ is clearly anti-bonding and at higher energy than the 1$\delta$. The
differences in the composition and relative energies of the 3σ and 1δ orbitals in NiO⁺ and NiS⁺ help to explain the observed differences between the ions’ electronic structures.

2.4 Conclusions

We find the bond strengths of NiO⁺ ($D_0 = 244.6 \pm 2.4 \text{ kJ/mol}$) and NiS⁺ ($D_0 = 240.3 \pm 1.4 \text{ kJ/mol}$) are very close to each other; previous reports indicated a larger difference, overestimating $D_0 (\text{NiO}^+)$. The proximity of the bond energies is likely due to a cancelling out of the effects of contributions from strongly bonding and strongly antibonding occupied orbitals in NiO⁺ versus weakly bonding and weakly antibonding occupied orbitals in NiS⁺. The photodissociation spectrum of NiO⁺ from 20350 to 29200 cm⁻¹ is weak, very broad and provides little information, consistent with the lack of optically accessible excited electronic states near $D_0$ and the relatively low oscillator strength of transitions to accessible states near the Ni⁺ ($^4\text{F}$) threshold. The spectrum of NiS⁺ from 19900 to 23200 cm⁻¹ exhibits a clear vibrational progression of ~280 cm⁻¹ with complex sub-structure. The observed features are mostly due to two overlapping electronic transitions, from the $X^4\Delta_{7/2}$ ground state to the $4^4\Delta_{7/2}$ and $5^4\Delta_{7/2}$ states. The $3^4\Delta \leftarrow 1^4\Delta$ and $3^4\Sigma^- \leftarrow 1^4\Sigma^-$ transitions may also contribute to some of the lower energy features below 20700 cm⁻¹. The near-degeneracy of the $1^4\Sigma^-$ and $1^4\Delta$ states of NiS⁺, which in NiO⁺ are separated by 5600 cm⁻¹, is explained by the near energetic equivalence of the 3σ and 1δ orbitals. Two peaks in the NiS⁺ spectrum have been assigned to hot bands likely originating from the $1^4\Sigma_{3/2}^-$ and $1^4\Sigma_{1/2}^-$ states as determined from temperature dependent spectra and confirmed by images of the Ni⁺ photofragments on each of the suspected ‘hot’ peaks. NiO⁺ photofragment images indicate that below the Ni⁺ ($^4\text{F}_j$) threshold, at 27778 cm⁻¹, NiO⁺
photodissociates to form Ni$^+$ ($^2D_1$) products in both spin-orbit levels, with higher-energy $J = 3/2$ products favored over $J = 5/2$. Above the Ni$^+$ ($^4F_j$) threshold, $^4F_{9/2}$ products dominate with each new spin-orbit level becoming less favored as it becomes energetically accessible. The Ni$^+$ ($^4F_j$) dissociation channels show vertical anisotropy, indicating rapid dissociation via a parallel transition, most likely the $3 \, ^4\Sigma^- \leftarrow X \, ^4\Sigma^-$. Only Ni$^+$ ($^2D_j$) + S ($^3P_i$) products are accessible at photon energies in the range of the NiS$^+$ spectrum, but the spin-orbit states of Ni$^+$ and S products are resolved in the images. We find that the first excited spin-orbit state of sulfur ($^3P_1$) is slightly favored over the ground spin-orbit state ($^3P_2$) in dissociation to Ni$^+$ ($^2D_{5/2}$) + S ($^3P_{1,2}$). The propensities for the first two Ni$^+$ spin-orbit states show the opposite trend, with lower energy Ni$^+$ ($^2D_{5/2}$) + S ($^3P_3$) products slightly favored over Ni$^+$ ($^2D_{3/2}$) + S ($^3P_2$) products. The latter trend is also the reverse of that observed in dissociation of NiO$^+$ to Ni$^+$ ($^2D_{5/2,3/2}$) + O ($^3P_3$).
Figure 2.1. Potential energy curves for $^4\Sigma^-$ and $^4\Pi$ electronic states of NiO$^+$ with vertical excitation energies below 40000 cm$^{-1}$ calculated at the MRCI+Q/aug-cc-pVQZ level.
Figure 2.2. Photodissociation spectrum of NiO$^+$ from 20350 to 29200 cm$^{-1}$. The spectrum was not recorded over the range of 23148 to 23385 cm$^{-1}$. 

![Photodissociation spectrum of NiO$^+$](image-url)
Figure 2.3. Photofragment image of Ni⁺ made by dissociating NiO⁺ at 27778 cm⁻¹ and the corresponding velocity distribution converted to total kinetic energy release. All NiO⁺ images were collected with the ion trap at 55 K and with He buffer gas. The image shown has been top/bottom and left/right symmetrized. Laser polarization is vertical (white arrow).
Figure 2.4. Photofragment images of Ni$^+$ made by dissociating NiO$^+$ at 29197 (i), 30769 (ii), and 31646 (iii) cm$^{-1}$ and the corresponding velocity distributions converted to total kinetic energy release. The images shown have been top/bottom and left/right symmetrized. Laser polarization is vertical (white arrows). Product state reference points along the TKER axis (red vertical lines) are calculated by subtracting the measured $D_0$ (20450 cm$^{-1}$) and individual product state energies from the photolysis energy. Groups of three lines with labeled fractional J values indicate Ni$^+$ ($^4F$) spin-orbit states, while single lines within a group indicate O atom spin-orbit states. Reference points are not absolute assignments, as O atom spin-orbit states are not resolved.
Figure 2.5. Photofragment image of Ni\(^+\) made by dissociating NiO\(^+\) at 30075 cm\(^{-1}\) and the corresponding velocity distribution converted to total kinetic energy release. The image shown has been top/bottom and left/right symmetrized. Laser polarization is vertical (white arrow). Product state reference points along the TKER axis (red vertical lines) are calculated by subtracting the measured \(D_0\) (20450 cm\(^{-1}\)) and individual product state energies from the photolysis energy. Groups of three lines reference Ni\(^+\) spin-orbit states, while single lines within a group reference O atom spin-orbit states. Reference points are not absolute assignments, as O atom spin-orbit states are not resolved.
Figure 2.6. Plot of photolysis energy – photoproduct energy (relative to ground state photoproducts) versus total kinetic energy release for several images of Ni\(^{+} (^{4}F_J)\) products resulting from photodissociation of cold NiO\(^{+}\). The bond dissociation energy \((D_0)\) of NiO\(^{+}\) is obtained from the y-intercept of the linear fit (20450 ± 200 \(\text{cm}^{-1}\), 244.6 ± 2.4 \(\text{kJ/mol}\)). The vertical error bars are due to not resolving the O atom spin-orbit states.
Table 2.1. Experimental and Theoretical Ground State Bond Dissociation Energies ($D_0$) of NiO$^+$ ($^4\Sigma^-$).

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$ (kJ/mol)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$^+$</td>
<td>260.7 ± 6.6</td>
<td>ion beam$^{32}$</td>
</tr>
<tr>
<td></td>
<td>254 ± 19</td>
<td>ion beam$^{33}$</td>
</tr>
<tr>
<td></td>
<td>244.6 ± 2.4</td>
<td>VMI (present study)</td>
</tr>
</tbody>
</table>

| NiO$^+$ | 249            | MRCI-L+DKH2+Q$^{29}$ |
|         | 239            | MRCI+DKH2+Q$^{29}$ |
|         | 241            | ACPF+DKH2$^{29}$ |
|         | 228            | MR-SDCI$^{28}$ |
|         | 225            | B3LYP$^{35}$ |
Figure 2.7. Potential energy curves for \( ^4\Sigma^- \), \( ^4\Pi \), \( ^4\Delta \), \( ^4\Phi \), and \( ^4\Gamma \) states of NiS\(^+\) that correlate to ground and first excited state products calculated at the MRCI+Q/aug-cc-pVQZ level. Calculations use the expanded d space in the MCSCF.
Table 2.2. Electronic states of NiS\(^+\) at the MRCI+Q/aug-cc-pVQZ level. Calculations use the expanded d space in the MCSCF. Vibrational frequencies and anharmonicities calculated by numerically solving the 1D Schrödinger equation and fitting the energy spacings of the lowest five vibrational levels. These are all of the quartet states that correlate to ground state or first excited state products (Ni\(^+\) (\(^2\)D, \(^4\)F) + S (\(^3\)P)).

<table>
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<th>State</th>
<th>(E)</th>
<th>(T_0)</th>
<th>(\tau_e)</th>
<th>(\omega_e)</th>
<th>(\omega_{\epsilon})</th>
<th>(\tilde{f}(\text{1}^4\Sigma^-))</th>
<th>(\tilde{f}(\text{1}^4\Delta))</th>
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<td>20343</td>
<td>2.40</td>
<td>240.2</td>
<td>-14.5</td>
<td>-</td>
<td>0.0079</td>
</tr>
<tr>
<td>(5^4\Pi)</td>
<td>25346</td>
<td>21875</td>
<td>2.61</td>
<td>138.2</td>
<td>-10.2</td>
<td>0.0002</td>
<td>0.0003</td>
</tr>
<tr>
<td>(6^4\Pi)</td>
<td>28531</td>
<td>22181</td>
<td>2.50</td>
<td>499.1</td>
<td>23.1</td>
<td>0.0023</td>
<td>0.0011</td>
</tr>
<tr>
<td>(3^4\Phi)</td>
<td>30973</td>
<td>23631</td>
<td>2.64</td>
<td>176.5</td>
<td>-3.5</td>
<td>-</td>
<td>0.0015</td>
</tr>
<tr>
<td>(3^4\Sigma^+)</td>
<td>29251</td>
<td>24776</td>
<td>2.67</td>
<td>195.6</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 2.8. Potential energy curves for $^4\Sigma^-$, $^4\Delta$, and $^4\Gamma$ states of NiS$^+$ that correlate to ground and first excited state products calculated at the MRCI+Q/aug-cc-pVQZ level. Calculations use the expanded d space in the MCSCF.
Figure 2.9. Potential energy curves for $^4\Pi$, and $^4\Phi$ states of NiS$^+$ that correlate to ground and first excited state products calculated at the MRCI+Q/aug-cc-pVQZ level. The two lowest energy states (1 $^4\Sigma^-$ and 1 $^4\Delta$) are shown for reference. Calculations use the expanded d space.
Figure 2.10. Potential curves for the lowest three electronic states of NiS\(^{+}\), including spin-orbit effects. Energies are at the MRCI+Q/aug-cc-pVQZ level, using (12e-, 9 MO) active space for MCSCF, allowing promotions from the 3s on S in the MRCI.
Figure 2.11. Photodissociation spectrum of NiS$^+$ near the Ni$^+$ ($^2$D) photofragment threshold under various conditions: supersonic expansion$^{30}$ (black solid); thermalized in a 3D quadrupole ion trap at 80 K with deuterium buffer gas (blue solid); thermalized in the ion trap at 291 K with helium buffer gas (red solid). Total simulated spectrum (red dash) and individual contributions from $\Sigma \leftarrow \Sigma$ and $\Delta \leftarrow \Delta$ transitions (blue and green dash, respectively) shifted by 2130 cm$^{-1}$ to lower energy are shown at the bottom. The simulations use a 50 cm$^{-1}$ FWHM Gaussian. Intensities in the total simulated spectrum are multiplied by 3 for easier visualization. 1$^*$ and 2$^*$ labels denote suspected spin-orbit hot bands, and 3 denotes the lowest energy peak assigned to a transition originating from the ground state.
Figure 2.12. Photofragment image of Ni$^+$ made by dissociating NiS$^+$ at 20631 cm$^{-1}$ and the corresponding velocity distribution converted to total kinetic energy release. All NiS$^+$ images were collected with the ion trap at 80 K and with D$_2$ buffer gas. The image shown has been top/bottom and left/right symmetrized. Laser polarization is vertical (white arrow). Product state reference points along the TKER axis (red vertical lines) are calculated by subtracting the measured $D_0$ (20090 cm$^{-1}$) and individual product state energies from the photolysis energy. Since S atom spin-orbit states are resolved, reference points also serve as assignments.
Figure 2.13. Photofragment image of Ni$^+$ made by dissociating NiS$^+$ at 21706 cm$^{-1}$ and the corresponding velocity distribution converted to total kinetic energy release. The image shown has been top/bottom and left/right symmetrized. Laser polarization is vertical (white arrow). Product state reference points along the TKER axis (red vertical lines) are calculated by subtracting the measured $D_0$ (20090 cm$^{-1}$) and individual product state energies from the photolysis energy.
Figure 2.14. Plot of photolysis energy – photoproduct energy (relative to ground state photoproducts) versus total kinetic energy release for several images of Ni$^+$ products resulting from photodissociation of cold NiS$^+$. The bond dissociation energy ($D_0$) of NiS$^+$ is obtained from the y-intercept of the linear fit ($20090 \pm 120$ cm$^{-1}$, $240.3 \pm 1.4$ kJ/mol).
Table 2.3. Experimental and Theoretical Ground State Bond Dissociation Energies ($D_0$) of NiS$^+$. 

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$ (kJ/mol)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS$^+$</td>
<td>251 ± 21</td>
<td>photodissociation$^{47}$</td>
</tr>
<tr>
<td></td>
<td>$\leq 238 \pm 4$</td>
<td>photodissociation$^{30}$</td>
</tr>
<tr>
<td></td>
<td>237 ± 4</td>
<td>ion beam$^{34}$</td>
</tr>
<tr>
<td></td>
<td>240.3 ± 1.4</td>
<td>VMI (this work)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS$^+$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Figure 2.15. Bond dissociation energies of 3d transition metal oxide (red) and sulfide (blue) cations (plotted from values in Table 2.4).
Table 2.4. Experimental Bond Dissociation Energies of MO$^+$ and MS$^+$.

<table>
<thead>
<tr>
<th>M$^+$ Species</th>
<th>$D_0$ (MO$^+$) (kJ/mol)</th>
<th>Ref. for MO$^+$</th>
<th>$D_0$ (MS$^+$) (kJ/mol)</th>
<th>Ref. for MS$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$^+$</td>
<td>689 ± 5</td>
<td>39</td>
<td>480 ± 5</td>
<td>44</td>
</tr>
<tr>
<td>Ti$^+$</td>
<td>664 ± 7</td>
<td>38</td>
<td>457 ± 7</td>
<td>44</td>
</tr>
<tr>
<td>V$^+$</td>
<td>584.0 ± 0.2</td>
<td>42</td>
<td>359 ± 9</td>
<td>43</td>
</tr>
<tr>
<td>Cr$^+$</td>
<td>357 ± 5</td>
<td>36</td>
<td>259 ± 16</td>
<td>45</td>
</tr>
<tr>
<td>Mn$^+$</td>
<td>242 ± 5</td>
<td>41</td>
<td>243 ± 23</td>
<td>45</td>
</tr>
<tr>
<td>Fe$^+$</td>
<td>339.6 ± 2</td>
<td>40</td>
<td>297 ± 4</td>
<td>46</td>
</tr>
<tr>
<td>Co$^+$</td>
<td>320 ± 6</td>
<td>32</td>
<td>285 ± 9</td>
<td>46</td>
</tr>
<tr>
<td>Ni$^+$</td>
<td>244.6 ± 2.4</td>
<td>this work</td>
<td>240.3 ± 1.4</td>
<td>this work</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>131.2 ± 4</td>
<td>14</td>
<td>200 ± 14</td>
<td>34</td>
</tr>
<tr>
<td>Zn$^+$</td>
<td>161 ± 5</td>
<td>37</td>
<td>198 ± 12</td>
<td>34</td>
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Figure 2.16. Molecular orbital diagrams for the 1 \(^4\Sigma^-\) states of NiS\(^+\) and NiO\(^+\). Orbitals are from the state-averaged CAS-SCF/aug-cc-pVQZ calculations. Relative energies of the orbitals are not to scale. Isosurfaces are drawn at 0.05. For the 3\(\sigma\) orbital for NiO\(^+\), isosurfaces at slightly larger values show that it is clearly anti-bonding.
CHAPTER 3
1- AND 2-PHOTON DISSOCIATION PATHWAYS OF THE MAGNESIUM IODIDE CATION

3.1 Introduction

Interactions and reactions within alkali and alkaline earth metal ion – ligand complexes have been studied by a wide variety of mass spectrometric techniques as they can be dissociated by collisions or, by taking advantage of their strongly absorbing atomic transitions in the visible and UV, can be probed by photodissociation, or “half-collisions”. Magnesium cation (Mg$^+$) complexes have received significant attention by groups employing the latter method with laser photolysis near the 280 nm Mg$^+$ $^2P_{1/2, 3/2} \leftarrow ^2S_{1/2}$ ($3p \leftarrow 3s$) transitions. Duncan and coworkers$^{76–79}$ and Beyer and coworkers$^{80–82}$ have measured photodissociation of solvated Mg$^+$ complexes such as Mg$^+$($H_2O$)$_n$ and Mg$^+$(CO$_2$)$_n$ obtaining detailed information on photochemical pathways, geometries, and spectroscopic parameters in these systems. In parallel, other groups have focused on complexes of Mg$^+$ with various organic molecules,$^{83–93}$ with photoinitiated C-H activation by Mg$^+$ reported in certain cases.

Although they do not observe C-H activation, Misaizu and co-workers report several other interesting photodissociation pathways in their studies of Mg$^+$ - XCH$_3$ complexes ($X = F$, Cl, Br, I).$^{87,88,90,91}$ In photolysis of Mg$^+$(ICH$_3$) from 24000 to 44000 cm$^{-1}$, for example, the authors observe energy-dependent competition between reaction products where the charge is retained on the metal (Mg$^+$, MgI$^+$) and ones where charge transfer occurs to the non-metal fragment (I$^+$, ICH$_3^+$).$^{87}$ In later studies, in addition to mass
spectrometrically detecting the charged products, they measured photofragment images,\textsuperscript{94,95} allowing them to determine the fragment anisotropy and kinetic energy release (KER).\textsuperscript{12,50,52} For linear molecules, $\Delta \Lambda=0$ transitions lead to parallel anisotropy ($\beta=2$ to 0) and $\Delta \Lambda=\pm 1$ are perpendicular ($\beta=-1$ to 0), with values near 2 and –1 corresponding to dissociation occurring faster than a rotational period. However, the Mg-I-C bond angle in Mg\textsuperscript{+}-ICH\textsubscript{3} is calculated\textsuperscript{95} to be 101°, so interpretation of the anisotropy is not as straightforward as it is for a linear molecule. Perpendicular anisotropy is observed in images of MgI\textsuperscript{+} fragments at 266 nm, revealing that the transition dipole moment is perpendicular to the dissociation axis (roughly the I – CH\textsubscript{3} bond axis) and parallel to the Mg – I bond axis.\textsuperscript{95} This indicates that photodissociation occurs via promotion of the Mg 3s electron to a 3p orbital aligned with the Mg-I bond.

Measurement of KER from a fragment image reveals how energy is distributed to the photofragments at a particular photolysis energy ($h\nu$):

$$h\nu + E_{\text{int}}(AB^+) = D_0(A^+-B) + \text{KER} + E_{\text{int}}(A^+) + E_{\text{int}}(B)$$ \hspace{1cm} (1)

If the ions start internally cold ($E_{\text{int}}(AB^+)=0$), then the maximum kinetic energy release gives an upper bound to the bond dissociation energy ($D_0(A^+-B)$). In small systems, there are few possible quantum states for the fragments, so a significant fraction are likely to be formed in their ground states. In this case, measuring the KER can give very precise bond strengths. In addition, the observed values of the KER can determine the electronic,\textsuperscript{41} spin-orbit\textsuperscript{96} and vibrational\textsuperscript{15} states of the photofragments ($E_{\text{int}}(A^+)$, $E_{\text{int}}(B)$). In some cases, photofragment imaging reveals that the ions have more energy than expected – that is, they
are not internally cold immediately prior to photodissociation. This can be due to hot ions \((E_{\text{int}}(\text{AB}^+)>0)\), in which case the measured KER can give information on low-lying vibrationally or electronically excited states. It can also be due to absorption of more than one photon, as in resonance enhanced photodissociation (REPD). This process is suggested to be responsible for the observed photodissociation spectra of ions such as Mg\(^+(\text{H}_2\text{O})\), Ca\(^+(\text{H}_2\text{O})\) and Mn\(^+(\text{H}_2\text{O})\) in which one photon is absorbed via a strong electronic transition to form an excited state whose predissociation lifetime is much longer than its fluorescence lifetime. Absorption of a second photon then leads to the observed photodissociation.

Although small linear molecules are well-suited to imaging experiments, diatomic molecules are the ideal candidates. Magnesium halides and isoelectronic group 13 metal-containing ions are of interest in fundamental physics research such as laser cooling and quantum computing, and happen to possess excellent kinematics for imaging. Although neutral MgI has been extensively characterized via electronic and rotational spectroscopy, there have been no previous experimental studies of the cation. Recently, Korek and coworkers published the first extensive theoretical study of this molecule, performing high-level \textit{ab initio} multi-reference configuration interaction (MRCI) calculations on MgI\(^+\) and other magnesium halide cations to determine their electronic structures and transition dipole moments from their ground electronic states. Further work to understand the fundamental properties of MgI\(^+\), including measurement of its bond energy, electronic spectrum and fragmentation pathways, may help inform on the dynamics in photoinitiated intra-cluster reactions observed in metal ion – organic halide complexes. In this work, we report calculated MRCI potential energy curves,
photodissociation spectra and photofragment images for visible and UV photodissociation of MgI⁺.

3.2 Theoretical Methods

Calculations of the ground and several excited electronic states of MgI⁺ were carried out using the MOLPRO software package\textsuperscript{58,59} at the following levels of theory: complete active space self-consistent field (CASSCF), multi-reference configuration interaction (MRCI), and with spin-orbit interactions included (MRCI+so). The basis set is cc-pVTZ for Mg and cc-VTZ-PP (including 28 electron relativistic effective core potential) for I. Calculations up to the MRCI level are very similar to those of Korek and coworkers.\textsuperscript{106} All calculations are carried out using C\textsubscript{2v} symmetry, so Σ⁺ and Δ states are A\textsubscript{1}; Π states are B\textsubscript{1} and B\textsubscript{2} and Σ⁻ and Δ states are A\textsubscript{2}. The CASSCF active space was initially selected to consist of the 3s orbital on Mg and 4d, 5s and 5p on I. Populations of each of the 4d (I) and 5s (I) MO’s were very close to 2, so they were removed from the active space and the higher-lying 3p (Mg) orbitals (with some contribution from 6s on I) added. The final calculations used 8 A\textsubscript{1} + 3 B\textsubscript{1} + 3B\textsubscript{2} + 0 A\textsubscript{2} closed orbitals (fully populated) and an active space of 3 A\textsubscript{1} + 2 B\textsubscript{1} + 2B\textsubscript{2} + 1 A\textsubscript{2} orbitals (8 electrons in 9 orbitals). The calculations are state-averaged and simultaneously include 4A\textsubscript{1}, 3B\textsubscript{1}, 3B\textsubscript{2} and 2A\textsubscript{2} singlet states and 3A\textsubscript{1}, 3B\textsubscript{1}, 3B\textsubscript{2} and 2A\textsubscript{2} triplet states. The B\textsubscript{1} and B\textsubscript{2} states are given half the weight of the A\textsubscript{1} and A\textsubscript{2} states. For the MRCI, the active space is expanded to also allow promotions from the highest-lying doubly occupied A\textsubscript{1} orbital (5s on I). The default, internally contracted (icMRCI) method was used. Spin-orbit calculations that
simultaneously included all of the aforementioned states were carried out using the MRCI wave functions and energies and the Breit–Pauli spin–orbit operator for internal configurations and a mean-field one-electron Fock operator for external configurations.

3.3 Results and Discussion

3.3.1 Electronic Structure of MgI⁺

Korek and co-workers recently carried out high level multireference configuration interaction, with Davidson correction (MRCI+Q) calculations on MgI⁺ as well as on other magnesium monohalides, calculating potential energy curves and transition dipole moment curves for many electronic states, and deriving the corresponding spectroscopic constants. They report a \( ^{1}\Sigma^{+} \) ground state with \( D_e = 205.8 \text{ kJ/mol} \) and \( r_e = 2.478 \text{ Å} \) and calculate ten singlet and twelve triplet excited electronic states. They also calculated transition dipole moments for transitions to several excited states: the \( ^{1}\Pi \) (\( T_e = 12653 \text{ cm}^{-1} \), \( \mu_e = 0.5 \text{ a.u.} \)), \( ^{2}\Sigma^{+} \) (31740 cm\(^{-1} \), 1.3 a.u.), \( ^{2}\Sigma^{+} \) (43104 cm\(^{-1} \), 1.8 a.u.), and \( ^{2}\Pi \) (46096 cm\(^{-1} \), 0.2 a.u.). We also carried out MRCI+Q calculations on MgI⁺ using the Molpro program\(^{58,59}\) and extended the study of Korek and co-workers by including spin-orbit effects, which are large for MgI⁺ and significantly affect many of the excited states. States are labeled by the total angular momentum along the internuclear axis, \( \Omega \). Inclusion of spin-orbit effects has negligible effect on the ground state, which is the \( (1) \Omega = 0^+ \) state, is 99% composed of the \( ^{1}\Sigma^{+} \) state, and has \( r_e = 2.49 \text{ Å} \). Electronic transitions from the ground state are optically allowed (one-photon) to states with \( \Omega = 0^+ \) (parallel) and 1 (perpendicular). Spectroscopic parameters for these states are listed in Table 3.1 and the potentials are displayed in Figure
3.1. The excited states have longer bonds and lower vibrational frequencies than the ground state. It is noteworthy that inclusion of spin-orbit effects not only shifts the positions of excited states, but also makes previously forbidden transitions optically allowed. For example, transitions to the (2) 0+ and (4) 0+ states are predicted to be quite intense, although they are primarily comprised of the (1) 3Π and (1) 3Σ+ states, respectively. Table 3.2 summarizes the properties of states with Ω=0, 2 and 3 and their potentials are shown in Figure 3.2. While there are few electronic states below 30000 cm⁻¹, there are numerous states at higher energy, which leads to many avoided crossings at energies above ~38000 cm⁻¹ and bond lengths of 3-4 Å. This is due to the presence of several product channels, Mg + I⁺ (3P₀,1,2), Mg⁺* (3P₁₀,₁₂,₃₂) + I (3P₂) and Mg + I⁺* (3D₂), at calculated energies of 37000-52000 cm⁻¹. The excited states will be discussed in more detail in conjunction with the experimental results.

3.3.2 MgI⁺→ Mg⁺ + I Photodissociation

3.3.2.1 MgI⁺→ Mg⁺ + I Photodissociation Spectrum

From 18000 to 21500 cm⁻¹, slightly above the MRCI predicted bond dissociation energy, MgI⁺ photodissociates to form Mg⁺ + I fragments. Spectra are measured by scanning the photolysis laser while monitoring the Mg⁺ fragment signal. The spectrum (Figure 3.3) shows a broad peak centered at ~20000 cm⁻¹ with little to no structure, suggesting rapid dissociation from an unbound excited state. Figure 3.1 shows three optically accessible excited states from the ground (1) Ω=0⁺ state in this region. The (1) Ω=1 and (2) Ω=1 states are weakly bound and correlate to ground state products, while the (2) Ω=0⁺ state has a deeper well and correlates to ground state Mg⁺ and spin-orbit excited
iodine (I*, ²P½). The breadth of the spectrum in this region is consistent with direct
dissociation following absorption to the repulsive inner wall of the (1) Ω=1 and (2) Ω=1
states. These states have long Mg-I bonds and are formed by strong mixing of the Ω=1
components of the (1) ³Π and (1) ³Π states. A less likely pathway is absorption to the (2)
Ω=0+ state followed by ultrafast intersystem crossing to the Ω=1 states, though this
pathway would likely give rise to a more structured spectrum than observed. The photon
energy at the peak of the spectrum (19900 cm⁻¹) best corresponds to absorption to the (2)
Ω=1 state, at a vertical energy of 19330 cm⁻¹ in our calculations, while transitions to the (1)
Ω=1 state contribute more at lower energy.

3.3.2.2 Images of Mg⁺ Fragments

Photofragment images were taken by tuning the photolysis laser to selected
wavelengths along the photodissociation spectrum and gating on the Mg⁺ fragment at the
imaging detector. Figure 3.4 shows a photofragment image taken near the broad peak of
the spectrum in Figure 3.2. The fragment distribution shows clear horizontal anisotropy
(β = −0.7), consistent with the perpendicular (2) Ω=1←X (1) Ω=0+ transition predicted in
this region. The kinetic energy release (KER) distribution indicates formation of ground
state products with moderate KER, giving a rough estimate of D₀ (MgI⁺). The precision of
this value of limited by the rather large FWHM of the peak which results from the high
fragment KER. To improve precision, additional images were taken at lower excitation
energy (Figure 3.5). These images show ground state products with very low KER, giving
a D₀ measurement with excellent precision (203 ± 1.8 kJ/mol, 17000 ± 150 cm⁻¹).
Perpendicular anisotropy (β = −0.6) suggests that the (1) Ω=1←X (1) Ω=0+ transition is
involved near the dissociation threshold, with a similar excited state lifetime. Image anisotropy also indicates that the parallel \( \Omega=0^+ \leftarrow (1) \Omega=0^+ \) transition does not contribute significantly to the photodissociation spectrum. However, the \( (2) \Omega=0^+ \leftarrow (1) \Omega=0^+ \) transition likely results in strong absorption without photodissociation since it is predicted to be more intense than the \( (1) \Omega=1 \leftarrow (1) \Omega=0^+ \) transition.

3.3.3 MgI\(^+ \) → I\(^+ \) + Mg Photodissociation

3.3.3.1 MgI\(^+ \) → I\(^+ \) + Mg Photodissociation Spectrum

In order to probe dissociation dynamics in the higher energy region of the potential energy surfaces of MgI\(^+ \), the photodissociation spectrum was measured from 33000 to 41000 cm\(^{-1} \) (Figure 3.6). As \( D_0(\text{MgI}^+) = 17000 \text{ cm}^{-1} \) and the ionization energy of I exceeds that of Mg by 22624 cm\(^{-1} \), only formation of Mg\(^+ \) + I is expected from 33000 to 39600 cm\(^{-1} \); above 39600 cm\(^{-1} \), both Mg\(^+ \) + I and Mg + I\(^+ \) channels are predicted to be active. Surprisingly, exclusively I\(^+ \) photofragments are formed over this entire range of the spectrum. One possible explanation for this observation is (a) that a significant portion of the parent ions are in a long-lived excited electronic state prior to photolysis; an electronic state above the threshold for I\(^+ \) is accessed by UV excitation from this lower-lying excited state, leading to I\(^+ \) + Mg products. A second possibility is (b) that I\(^+ \) photofragments are formed via a two-photon process, resonance enhanced photodissociation (REPD), in which absorption of one photon produces MgI\(^+ \) in a long-lived excited electronic state; these excited molecules then absorb a second photon and dissociate to form Mg + I\(^+ \). Since analysis of photofragment images of MgI\(^+ \) (discussed in detail in section 3.3.3.2) overwhelmingly points to (b) as the mechanism for photolysis in the UV, the discussion
below assumes the spectrum arises entirely from photolysis of ground $((1) \Omega = 0^+)$ state \( \text{MgI}^+ \).

The \( \text{MgI}^+ \rightarrow \text{I}^+ + \text{Mg} \) photofragment spectrum (Figure 3.6) from 33000 to 38500 cm\(^{-1}\) is highly structured with two underlying broad features, centered at 33800 and 38800 cm\(^{-1}\). The spacing of peaks between 33000 and 35500 cm\(^{-1}\) is more irregular than the rest of the structured part of the spectrum, with a minimum of \(\sim 80 \text{ cm}^{-1}\) and a maximum of \(\sim 230 \text{ cm}^{-1}\). There are \(\sim 10\) major peaks between 35500 and 38500 cm\(^{-1}\) that are consistent with a regular vibrational progression; these are spaced by an average of 227 cm\(^{-1}\). The peaks in this region generally become broader with increasing photon energy, and above 38500 cm\(^{-1}\) the spectrum is unstructured.

Calculated potential energy curves for \( \text{MgI}^+ \) (Figure 3.1) show allowed transitions to two excited states from the \((1) \Omega=0^+\) ground state in the region of the measured UV photofragment spectrum (33000 to 41000 cm\(^{-1}\)). A parallel transition to the \((3) \Omega=0^+\) state with \(T_0 = 31552 \text{ cm}^{-1}\) is predicted at a vertical transition energy of 34535 cm\(^{-1}\) while a perpendicular transition to the \((4) \Omega=1\) state with \(T_0 = 37401 \text{ cm}^{-1}\) is predicted at a vertical transition energy of 39280 cm\(^{-1}\) (Table 3.1). The \((3) \Omega=0^+ \leftrightarrow (1) \Omega=0^+\) transition should be far more intense \((f = 0.197)\) than the \((4) \Omega=1 \leftrightarrow (1) \Omega=0^+\) \((f = 7.6 \times 10^{-4})\); the vibrational frequency \((\omega_c = 218 \text{ cm}^{-1})\) of the \((3) \Omega=0^+\) is also more consistent with the experimental spectrum \((\omega = 227 \text{ cm}^{-1})\) than that of the \((4) \Omega=1\) \((\omega_c = 267 \text{ cm}^{-1})\) (Table 3.1). A Franck-Condon simulated spectrum for the \((3) \Omega=0^+ \leftrightarrow (1) \Omega=0^+\) transition from both \(v=0\) (blue dash) and \(v=1\) (red dash) in the ground electronic state is shown below the experimental spectrum in Figure 3.6; intensities are calculated assuming equal populations in \(v''=0\) and
Simulated spectra imply most peaks between 33000 and 34000 cm\(^{-1}\) and between 37000 and 38500 cm\(^{-1}\) come from \(v''=1\), and most peaks between 35000 and 36000 cm\(^{-1}\) come from \(v''=0\); between 34000 and 35000, and 36000 and 37000 cm\(^{-1}\), peaks come from both vibrational levels. The simulation is of the one-photon absorption spectrum. The observed intensities in the photodissociation spectrum would also be affected by the cross section for absorption of a second photon and by the subsequent photodissociation yield.

The one-photon absorption spectrum of MgI\(^+\) from 33000 to 38500 cm\(^{-1}\) is expected to be far more intense overall than the region above 38500 cm\(^{-1}\); it is worth noting that this is the opposite of what is observed in the photodissociation spectrum. The broad feature centered at 38700 cm\(^{-1}\) has the highest intensity in the spectrum. This feature lines up very closely with the energy of the barrier to dissociation of the (3) \(\Omega=0^+\) state at \(r = 3.8 \, \text{Å}\) (Figure 3.1). It is therefore possible that this peak arises from both two-photon dissociation of MgI\(^+\) and one-photon dissociation of vibrationally hot MgI\(^+\). In fact, increasing favorability of the one-photon process with increasing photon energy is consistent with the broadening of the spectrum, as direct dissociation is accessible once the barrier of the (3) \(\Omega=0^+\) is overcome energetically. The higher efficiency of one-photon rather than two-photon dissociation also explains the increase in intensity.

### 3.3.3.2 Images of I\(^+\) Fragments

Photofragment images of I\(^+\) were collected by gating on the I\(^+\) fragment and tuning the ion optics voltages for optimal resolution. As the heavier fragment is imaged, the kinematics are much less favorable than when detecting Mg\(^+\), leading to poorer kinetic energy resolution. Figure 3.7 shows an I\(^+\) photofragment image taken at 36245 cm\(^{-1}\); this
photon energy corresponds to a sharp peak in the middle of the structured region of the photodissociation spectrum (Figure 3.6). The KER distribution has two peaks, at 3300 and 10100 cm⁻¹, corresponding to two different Mg + I⁺ fragment channels. The two lowest atomic states of Mg are separated by 21850 cm⁻¹, while the atomic ground state of I⁺ is split into three spin-orbit levels with relative energies of 0 (⁵P₂), 6448 (⁵P₀) and 7087 (⁵P₁) cm⁻¹. The lower energy peak in the KER distribution is thus due to both ⁵P₀ and ⁵P₁ fragments and the higher energy peak is from the ⁵P₂ fragments. I⁺ (⁵P₀,₁) fragments are favored over I⁺ (⁵P₂) fragments with a branching ratio of 1.4:1. The fragment distribution also shows near-limiting parallel anisotropy (inner channel, β= 1.3; outer channel, β= 1.5). Figure 3.8 shows a photofragment image taken at 33835 cm⁻¹, on a sharp feature near the onset of the spectrum. The KER distribution shows a single peak at 5400 cm⁻¹. This peak best corresponds to I⁺ (⁵P₂) fragments, but there is a significant discrepancy between the observed decrease in KER (4700 cm⁻¹) and the decrease in photon energy (2410 cm⁻¹) from the image in Figure 3.7 to the one in Figure 3.8.

The observed discrepancy in KER between images along with some energy accounting helps determine by which mechanism I⁺ fragments are formed at photon energies below the threshold for I⁺ fragments. From conservation of energy,

\[ E_{\text{photon}} \times n_{\text{photon}} + E_{\text{int}}(\text{MgI}^+) = D_0(\text{Mg-I}^+) + \text{KER} + E_{\text{int}}(\text{fragments}) \]  

(2)

or

\[ \text{KER} = E_{\text{photon}} \times n_{\text{photon}} + E_{\text{int}}(\text{MgI}^+) - D_0(\text{Mg-I}^+) - E_{\text{int}}(\text{fragments}) \]  

(3)

where \( E_{\text{photon}} \) is the energy of one photon, \( n_{\text{photon}} \) is the number of photons absorbed, \( E_{\text{int}}(\text{MgI}^+) \) is the initial internal energy in the MgI⁺ parent ion and the bond dissociation energy
(D_0(Mg-I^+)) is 17000 cm^{-1}. For fragments with the same internal energy, plotting KER as a function of the photon energy should give a line with slope n_{\text{photon}}. This analysis was carried out for nine I^+ fragment images, including the two shown in Figures 3.7 and 3.8, collected at photon energies for selected peaks in the photofragment spectrum shown in Figure 3.6. The results are shown in Figure 3.9. The best fit line has a slope of 1.97, indicating that the I^+ fragments are due to absorption of two photons. The next step is to determine which state of Mg is formed. If the internal energy in the MgI^+ parent ion is assumed to be zero, then the internal energy of the fragments is 45400 \pm 500 cm^{-1}. Production of ground state Mg + I^+ (^3P_J) corresponds to fragments with 22624 cm^{-1} of internal energy compared to Mg^* + I, due to the difference in ionization energies of atomic Mg and I. Thus, the Mg and/or I^+ fragments are electronically excited. The only excited states with the appropriate energy are the excited ^3P_J states of Mg, with energies of 21850 (J=0) to 21911 cm^{-1} (J=2). If these states are formed, then the internal parent energy calculated from the y-intercept of the plot is 900 \pm 1500 cm^{-1} indicating dissociation of ground electronic state ions. Thus, photodissociation in the 33600 to 36700 cm^{-1} region is due to resonance-enhanced two photon absorption and leads to Mg^* (^3P_J) + I^+ (^3P_J) products. Since the vibrational spacing in the ground state of MgI^+ is much smaller than the uncertainty in KER in the I^+ images, the linear fitting data do not, however, aid in assigning peaks in the photofragment spectrum arising from v''=0 or v''=1 in the ground state.

In images at photon energies above 37600 cm^{-1}, Mg^* (^3P_J) + I^+ (^3P_{2,0,1}) products are still formed at moderate to high KER, but a new low KER channel is also visible. The low KER fragments are consistent with the Mg^* (^3P_J) + I^+ (^1D_2) channel, which is predicted to open at 75210 cm^{-1} (a one photon energy of 37605 cm^{-1}). At photon energies above 38610
cm⁻¹, images change in appearance dramatically. There is virtually no fragment intensity at moderate or high KER and very high intensity at near-zero KER. In addition, the most probable KER for this channel does not increase with increasing photon energy from 38610 to 39447 cm⁻¹ (Figure 3.10). The channel to form ground state Mg + I⁺ products opens at an energy of 39600 cm⁻¹ relative to the ground state of MgI⁺, which is higher than the one-photon photolysis energy for these images. However, this channel can be accessed by photodissociation of vibrationally hot (ν”=1,2,3) MgI⁺ via a one-photon process; increasing photofragment yield of MgI⁺ in lower vibrational states with increasing photon energy is also consistent with constant KER observed in the images from 38610 to 39447 cm⁻¹. This analysis implies that a one-photon mechanism is favored over a two-photon mechanism at photon energies above 38610 cm⁻¹ and photodissociation of MgI⁺ from 38610 to 39447 cm⁻¹ is almost exclusively from a relatively small number of vibrationally excited parent ions.

The opportunity to observe REPD in MgI⁺ is largely due to the very inefficient dissociation of the (3) Ω=0⁺ state coupled with its short radiative lifetime of ~6 ns (based on the calculated oscillator strength), which greatly limits the time for indirect dissociation. There are several metal-containing ions in which similar photodissociation dynamics have been observed. For example, we estimate that the photodissociation quantum yield for Al₂⁺ near 40000 cm⁻¹ is only 0.006.⁵⁵ The photodissociation yield for Mg⁺(H₂O), Ca⁺(H₂O) and Mn⁺(H₂O) in the UV is much smaller than expected, and the signal is likely due to REPD.⁷⁶,⁹⁷,⁹⁸,¹⁰⁷ In all of these molecules, the electronic transition to the excited state (p → s on the metal) is strongly allowed (leading to a short radiative lifetime), the excited state is bound and so cannot directly dissociate, and non-radiative transitions to lower-lying electronic states are inefficient because there are few excited states at nearby energies. As
demonstrated in this work, measuring photofragment KER by imaging can confirm suspected cases of REPD when spectroscopic data are inconclusive or merely suggestive of it.

3.4 Conclusions

From ground state Mg\(^+\) (\(^3S\)) + I (\(^3P_{3/2}\)) product KER distributions in MgI\(^+\) photofragment images near threshold, we report the first experimental measurement of the MgI\(^+\) bond strength (D\(_0\) = 203.0 ± 1.8 kJ/mol; 2.10 ± 0.02 eV). This value is slightly lower than the MRCI+Q calculated bond strength (D\(_0\) (MgI\(^+\)) = 205.8 kJ/mol). Perpendicular anisotropy in the images of the Mg\(^+\) (\(^3S\)) + I (\(^3P_{3/2}\)) products at photolysis energies between 17152 and 20619 cm\(^{-1}\) is consistent with a \(\Omega=1 \leftarrow (1) \Omega=0\) transition. The calculations indicate absorption to the (1) \(\Omega=1\) state is more likely at lower energy, and the (2) \(\Omega=1\) at higher energy in this region. Image anisotropy and the breadth of the photofragment spectrum from 17000 to 21500 cm\(^{-1}\) reveal that dissociation is prompt following excitation via these transitions. In agreement, the calculations show that vertical transitions from the ground state at these energies are to the excited states’ repulsive walls.

At higher photon energy, in the UV, Mg\(^+\) products with low KER are predicted, with the lowest energy I\(^-\) channel predicted to open at 39600 cm\(^{-1}\). However, I\(^-\) products are formed at photon energies as low as 33000 cm\(^{-1}\) and Mg\(^+\) products are not observed. Plotting observed KER versus photon energy for I\(^-\) fragment images at photon energies of 33000 to 37000 cm\(^{-1}\) yields a line of best fit with a slope of 1.97, indicating that the observed products are due to resonance enhanced two-photon dissociation, where Mg (\(^3P\)) + I\(^-\) (\(^3P_1\)) products are formed after absorption of a second photon from a bound excited state in the energy region corresponding to absorption of one photon. photofragment spectrum of MgI\(^+\)
\[ \rightarrow \text{Mg} + \text{I}^+ \text{ from 33000 to 37000 cm}^{-1} \text{ matches well with simulated spectra of the (3) } \Omega=0^+ \]

\[ \leftarrow \text{(1) } \Omega=0^+ \text{ transition from the } v=0 \text{ and } v=1 \text{ levels of the (1) } \Omega=0^+ \text{ state. Above 38500 cm}^{-1} \text{, the sharp peaks in the spectrum transition to broad features. While below 38000 cm}^{-1} \text{ images still show significant intensity at moderate and high KER, images above 38600 cm}^{-1} \text{ show only one channel at low KER. In the latter energy regime, KER does not increase with photon energy. The spectrum and images in this region can be explained by a one-photon dissociation mechanism to form } \text{Mg (S)} + \text{I}^+ (P_2) \text{ following absorption to the same (3) } \Omega=0^+ \text{ state, but possibly from higher vibrational levels of the (1) } \Omega=0^+ \text{ at lower energies and the ground vibrational level at higher energies.} \]
Figure 3.1. Potential energy curves for electronic states of MgI\(^+\) with \(\Omega=0^+\) and 1 and \(T_e\) values below 55000 cm\(^{-1}\) calculated at the MRCI level with spin-orbit and Davidson corrections and with the cc-pVTZ basis set. Vertical transition at 2.49 Å is shown with a dashed black line.
Table 3.1. Calculated spectroscopic parameters for $\Omega=0^+$ and $1^+$ states of MgI at the MRCI+Q+so/cc-pVTZ level. Energies in cm$^{-1}$. The permanent dipole moment $\mu$ is in atomic units, as is the transition dipole moment $\mu_{\text{e}}$ for radiative transitions from the (1) $0^+$ ground state. These values, and the composition in terms of $2\Sigma^+\Sigma$ states, are at $r=2.49$ Å.

a) The second number is the value of $\Omega$; the first is the number of the state with that value of $\Omega$. b) Double minimum state. c) Energies refer to quasi-bound (Feshbach resonance) states.

<table>
<thead>
<tr>
<th>State$^{a)}$</th>
<th>$E_{\text{vert}}$</th>
<th>$r_c$ (Å)</th>
<th>$T_0$</th>
<th>$\omega_c$</th>
<th>$\omega_{\text{ex}}$</th>
<th>$\mu_{\text{e}}$</th>
<th>$\mu$</th>
<th>Composition</th>
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<tr>
<td>(1) $0^+$</td>
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<td>2.49</td>
<td>0</td>
<td>368.0</td>
<td>1.5</td>
<td>-</td>
<td>4.73</td>
<td>99% $X^\Sigma^+$</td>
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<td>(2) $0^+$</td>
<td>19868</td>
<td>3.00</td>
<td>15917</td>
<td>194.0</td>
<td>-1.1</td>
<td>0.60</td>
<td>1.71</td>
<td>95% (1) $^3\Pi$</td>
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<tr>
<td>(3) $0^+$</td>
<td>34535</td>
<td>2.85</td>
<td>31483</td>
<td>218.3</td>
<td>-2.3</td>
<td>1.37</td>
<td>1.99</td>
<td>96% (2) $^1\Sigma^+$</td>
</tr>
<tr>
<td>(4) $0^+$</td>
<td>42744</td>
<td>2.81, 3.69</td>
<td>40031</td>
<td>168.0</td>
<td>3.5</td>
<td>0.58</td>
<td>2.29</td>
<td>91% (1) $^1\Sigma^+$</td>
</tr>
<tr>
<td>(5) $0^+$</td>
<td>48395</td>
<td>2.94</td>
<td>42228</td>
<td>226.0</td>
<td>4.7</td>
<td>1.71</td>
<td>2.42</td>
<td>76% (3) $^1\Sigma^+$</td>
</tr>
<tr>
<td>(1) $1^+$</td>
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<td>3.03</td>
<td>11049</td>
<td>196.1</td>
<td>5.4</td>
<td>0.38</td>
<td>1.59</td>
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<td>14236</td>
<td>152.4</td>
<td>4.4</td>
<td>0.39</td>
<td>1.61</td>
<td>53% (1) $^1\Pi$, 33% (1) $^3\Pi$</td>
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<td>21220</td>
<td>92.0</td>
<td>1.3</td>
<td>0.13</td>
<td>1.77</td>
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<td>37401</td>
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<td>41362</td>
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<td>(6) $1^+$</td>
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<td>41887</td>
<td>240.0</td>
<td>2.7</td>
<td>0.47</td>
<td>2.28</td>
<td>67% (1) $^1\Sigma^+$, 20% (2) $^1\Sigma^+$</td>
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</tbody>
</table>
Figure 3.2. Potential energy curves for electronic states of MgI$^+$ with $\Omega=0$, 2 and 3 and $T_e$ values below 55000 cm$^{-1}$ calculated at the MRCI level with spin-orbit and Davidson corrections and with the cc-pVTZ basis set.
Table 3.2. Calculated spectroscopic parameters for $\Omega=0$, 2 and 3 states of MgI$^+$ at the MRCI+so/cc-pVTZ level. Energies in cm$^{-1}$. The permanent dipole moment $\mu$ is in atomic units. These values, and the composition in terms of $\Sigma^+ \Sigma$ states, are at $r=2.49$ Å.

| State$^a$ | $E_{\text{vert}}$ (eV) | $r_c$ (Å) | $T_0$ | $\omega_x$ | $\omega_x \times c$ | $E_{\text{vert}, ||}$ (eV) | $\mu_\parallel$ ($\mu_\parallel$) | $\mu_\perp$ | Composition |
|-----------|----------------|----------|-------|-----------|----------------|------------------|------------------------|----------|-------------|
| (1) 0     | 18943          | 3.05     | 13945 | 166.7     | 5.1            | -                | -                      | 1.63     | 87% (1) $^3\Pi$ |
| (2) 0     | 28237          | 3.41     | 21109 | 94.8      | 1.2            | 7727.182         | 2.30                   | 2.77     | 87% (1) $^3\Sigma^+$ |
| (3) 0     | 39404          | 2.75     | 37940 | 256.4     | 2.3            | 24610.003        | 2.29                   | 2.77     | 77% (2) $^3\Sigma^+$, 23% (1) $^1\Sigma^-$ |
| (4) 0     | 43489          | 2.78     | 41253 | 236.7     | 1.0            | 28146.041        | 2.29                   | 2.77     | 71% (1) $^1\Sigma^-$, 19% (2) $^1\Sigma^+$ |
| (5) 0     | 53354          | 3.62$^{b)}$ | 46474 | 411.8     | 19.6          | 36460.082        | 2.43                   | 2.77     | 90% (2) $^3\Pi$ |
| (1) 2     | 15414          | 3.03     | 10714 | 199.1     | 4.8            | -                | -                      | 1.61     | >99% (1) $^3\Pi$ |
| (2) 2     | 39965          | 2.76     | 37794 | 245.0     | 1.5            | 27910.004        | 2.28                   | 2.77     | 59% (1) $^3\Delta$, 41% (1) $^1\Delta$ |
| (3) 2     | 43955          | 2.79     | 41625 | 245.3     | 6.4            | 31507.045        | 2.29                   | 2.77     | 53% (1) $^3\Delta$, 36% (1) $^3\Delta$ |
| (4) 2     | 53220          | 3.30$^{c)}$ | 44340 | 485.8     | 21.8          | 38314.021        | 2.27                   | 2.77     | 81% (2) $^3\Pi$ |
| (5) 2$^{e)}$ | 55919       | 3.03     | 50922 | 231.1     | 6.7            | 40373.249        | 2.14                   | 2.77     | 90% (3) $^3\Pi$ |
| (1) 3     | 39849          | 2.76     | 37829 | 251.8     | 2.0            | -                | 2.31                   | 2.77     | 100% (1) $^3\Delta$ |

a) The second number is the value of $\Omega$; the first is the number of the state with that value of $\Omega$.
b) Vertical energies from the lowest-energy state with the same value of $\Omega$. This is at $r=3.05$ Å for $\Omega=0$ states and $r=3.03$ Å for $\Omega=2$ states.
c) Transition dipole moment for radiative transitions from the lowest state with the same value of $\Omega$, in atomic units.
d) These states undergo multiple avoided crossings with nearby states and thus have two minima.
e) Energies refer to quasi-bound (Feshbach resonance) states.
Figure 3.3. Photodissociation spectrum of MgI→ Mg⁺ + I from 18000 to 21500 cm⁻¹. The spectrum was recorded after cooling the parent ion packet with He trap gas at a nominal trap temperature of 200 K.
Figure 3.4. Photofragment image of Mg\(^+\) fragments resulting from photodissociation of MgI\(^+\) at 20619 cm\(^{-1}\) (laser polarization vertical) and corresponding total KER distribution.
Figure 3.5. Photofragment images of Mg$^+$ fragments resulting from photodissociation of MgI$^+$ at 17152 cm$^{-1}$ with laser polarization horizontal (left) and vertical (right), and corresponding total KER distribution (bottom).
Figure 3.6. Photodissociation spectrum of MgI$^+$ → I$^+$ + Mg from 33000 to 40000 cm$^{-1}$. Simulated spectra of the (3) $\Omega=0^+ \leftarrow (1) \Omega=0^+$ from the ground (blue) and first excited (red) vibrational state of the (1) $\Omega=0^+$ state are shown under the experimental spectra (black). Simulated spectra are shifted higher in energy by 1180 cm$^{-1}$ and peaks are shown as 50 cm$^{-1}$ FWHM Gaussians. The spectrum is measured with He buffer gas at a nominal trap temperature of 200 K.
Figure 3.7. Photofragment images of I⁺ fragments resulting from photodissociation of MgI⁺ at a photon energy 36245 cm⁻¹ (laser polarization vertical) and corresponding total KER distribution.
Figure 3.8. Photofragment images of I\(^+\) fragments resulting from photodissociation of MgI\(^+\) at a photon energy of 33835 cm\(^{-1}\) (laser polarization vertical) and corresponding total KER distribution.
Figure 3.9. Plot of total kinetic energy release versus photon energy for several images of I$^+$ ($^3P_2$) products resulting from photodissociation of MgI$^+$ at photon energies in the structured region of the photodissociation spectrum. Error bars are ± half width at half maximum (HWHM) of the most probable KER peak for I$^+$ ($^3P_2$) products from each image. The slope of the line of best fit is shown above the data points.
Figure 3.10. Plot of total kinetic energy release versus photon energy for several images of I^+ products resulting from photodissociation of MgI^+ at photon energies between 38610 and 39447 cm\(^{-1}\). Error bars are ± half width at half maximum (HWHM) of the most probable KER peak from each image.
CHAPTER 4
SUMMARY AND FUTURE DIRECTIONS

4.1 Summary and Conclusions

Photofragment ion imaging is complemented with photofragment spectroscopy and ab initio calculations to determine the bond strengths and dissociation dynamics of the nickel oxide (NiO\(^+\)), nickel sulfide (NiS\(^+\)) and magnesium iodide (MgI\(^+\)) cations. This work establishes these molecules as benchmark systems and adds to the database of high precision, detailed experimental measurements of the fundamental properties of MX\(^+\). Photofragment imaging also enables assignment of dynamics that can’t be determined by spectroscopic methods, irrespective of whether the system is better suited to study by photodissociation or photodetection methods. The systems studied in this work represent three types of spectroscopically challenging cases: (1) weak absorption near D\(_0\) (2) moderate absorption near D\(_0\) leading to highly complex spectra and (3) strong absorption to a bound state correlating to energetically forbidden products, leading to REPD (resonance enhanced photodissociation).

Studies of NiO\(^+\) and NiS\(^+\) reveal how isoelectronic MX\(^+\) can have very different electronic structures and spectroscopy, and still have near-identical bond energies. The 3\(\sigma\) and 1\(\delta\) orbitals of NiO\(^+\) are separated in energy by more than those of NiS\(^+\); this explains why the 1 \(^4\Sigma^-\) and 1 \(^4\Delta\) states of NiS\(^+\) are near-degenerate while those of NiO\(^+\) are separated by 5600 cm\(^{-1}\). Calculations on NiO\(^+\) indicate there are no optically allowed transitions to states near the predicted D\(_0\), and those to states near the first excited state threshold (Ni\(^+\) \(\left(^4\text{F}\right) + \text{O} \left(^3\text{P}\right)\)) are predicted to be fairly weak. In agreement, photofragment spectra show that NiO\(^+\) dissociates broadly and with low to moderate fragment yield from 20350 to
29200 cm$^{-1}$. An image of Ni$^+$ fragments at 27778 cm$^{-1}$ shows moderate KER, indicative of ground state $^2$D$_J$ products, while images at and above 29197 cm$^{-1}$ show very low KER, indicative of excited $^4$F$_J$ products. The favorability of the $^4$F$_J$ spin-orbit channels upon dissociation decreases with increasing product state energy in all images where multiple channels are available. The images of $^4$F$_J$ products display vertical anisotropy, consistent with dissociation following a parallel $3^4\Sigma^+ \leftarrow X^4\Sigma^-$ transition. Transitions from the X $^4\Delta_{7/2}$ ground state to the $4^4\Delta_{7/2}$ and $5^4\Delta_{7/2}$ states comprise the majority of the NiS$^+$ photodissociation spectrum from 19900 to 23200 cm$^{-1}$. Two hot bands, the two lowest energy peaks in the spectrum, were assigned to transitions from the low-lying $1^4\Sigma_{3/2}^-$ and $1^4\Sigma_{1/2}^-$ states by temperature-dependent spectra, and NiS$^+$ photofragment images at the respective photon energies. In NiS$^+$ photofragment images at higher energy, both the Ni$^+$ ($^2$D$_J$) and S ($^3$P$_J$) spin-orbit states are resolved. Images show that lower energy spin-orbit product states of sulfur are preferred over higher energy ones; the reverse is true for the Ni$^+$ ($^2$D$_J$) product states. Bond dissociation energies measured by imaging in this work ($D_0 (\text{NiO}^+)=244.6 \pm 2.4 \text{ kJ/mol}, D_0 (\text{NiS}^+) = 240.3 \pm 1.4 \text{ kJ/mol}$) indicate that previous measurements$^{32,33}$ overestimated the NiO$^+$ bond strength. NiO$^+$ is calculated to have stronger bonding and antibonding occupied orbitals than NiS$^+$, likely contributing to the two ions’ similar bond strengths. The proximity of the bond strengths of the two ions provides the further insight that the differences in their reactivities with alkanes to form alcohols or thiols results instead from differences in the product O-H and S-H bond strengths.

Unlike for NiO$^+$ and NiS$^+$, studies of MgI$^+$ retrospectively show the species is best suited to study by fluorescence spectroscopy rather than photodissociation spectroscopy;
however, even in this case, imaging directly reveals the occurrence of a two-photon process that could not be easily assigned by spectroscopic methods. In the magnesium iodide cation (MgI\(^+\)), despite strong spin-orbit coupling opening otherwise forbidden transitions and dissociation pathways, the dominant, strongly allowed transition in the UV has an insufficient excited state lifetime for dissociation; this effect leads to a surprising preference for two-photon dissociation in this energy regime. In the visible regime, the dynamics are more straightforward. The photodissociation spectrum of MgI\(^+\) from 18000 to 21500 cm\(^{-1}\) shows a single broad peak centered at 20000 cm\(^{-1}\); images of Mg\(^+\) fragments in this region show ground state Mg\(^+\) (\(^2\)S) + I (\(^2\)P\(_{3/2}\)) products with perpendicular anisotropy. Calculations are consistent with the spectrum and images, indicating absorption to the repulsive inner walls of the (1) \(\Omega=1\) and (2) \(\Omega=1\) states from the ground (1) \(\Omega=0^+\) state leads to prompt dissociation at these energies. The bond strength of MgI\(^+\) (\(D_0 = 203.0 \pm 1.8\) kJ/mol; 2.10 ± 0.02 eV), as determined from the images of Mg\(^+\) (\(^2\)S) + I (\(^2\)P\(_{3/2}\)) products, is close to the MRCI+Q calculated value (\(D_0(MgI^+) = 205.8\) kJ/mol).

The photodissociation mechanism of MgI\(^+\) in the UV is less straightforward than in the visible. From 33000 to 40000 cm\(^{-1}\), only Mg + I\(^+\) fragments are observed in the photodissociation spectrum despite the lowest energy fragment channel for charge transfer lying at 39600 cm\(^{-1}\) above the MgI\(^+\) ground state. The observed fragments are thought to result from resonance enhanced two photon dissociation and are assigned to the Mg (\(^3\)P) + I\(^+\) (\(^3\)P\(_J\)) channel. This theory is supported by the value of the slope (1.97) of the best fit line for a plot of most probable KER vs. photon energy over nine images of I\(^+\) fragments. Calculations and simulations of the absorption spectrum at energies of 33000 to 37000 cm\(^{-1}\) predict a vibrational progression associated with transitions to the (3) \(\Omega=0^+\) state from
v=0 and v=1 of the MgI+ ground electronic state, consistent with the appearance of the photodissociation spectrum. Images of I+ fragments above 38610 cm\(^{-1}\) show very low KER that remains constant with increasing photon energy, suggesting Mg (\(^3\)S) + I+ (\(^3\)P\(^2\)) fragments may form following one-photon dissociation of vibrationally hot MgI+ at these energies.

The precise bond dissociation energies measured from the fragment radial distributions imaged in this work have important implications for understanding chemical bonding to metal ions. The proximity of the NiO+ and NiS+ bond strengths shows that Ni+ is the ‘crossing point’ in the series of first row transition metal cations, with respect to whether they bind to O or S more strongly. Since for first row transition M+ with a smaller atomic number than M=Ni, bonds to O and S are governed more by covalent interactions, and for those with a larger atomic number than M=Ni, bonding is more electrostatic than covalent, bonding of Ni+ with O and S likely has equal contributions from both types of interactions. The \(D_0\) (MgI+) value reported here represents, to the author’s knowledge, the first experimental measurement of an singly charged magnesium cation - halogen bond strength.

The photodissociation dynamics obtained from the fragment angular distributions and branching ratios continue to show the trend of favoring formation of electronically excited products over ground state products (or higher energy product states over lower energy ones). This trend is opposite what one would expect based on entropic considerations (translational vs. electronic degrees of freedom) and is also observed for two other systems previously studied with the imaging instrument: Al\(_2^+\) and MnO+. In contrast to the electronic propensities, product spin-orbit propensities in all three systems
presented here are much more unpredictable, ranging from low spin-orbit energy favored
\((\text{Ni}^+ (^4\text{F}_J) \text{ from NiO}^+)\), to high-spin orbit energy favored \((\text{Ni}^+ (^2\text{D}_J) \text{ from NiS}^+ \text{ and I}^+ (^3\text{P}_J) \text{ from MgI}^+)\). Additionally, for NiO\(^+\) in particular, comparison of image anisotropies to calculated potential energy curves not only enables determination of the transition dipole moment but also the predissociative behavior of the species; this can include (1) differentiating between direct dissociation from a repulsive state and rapid dissociation from a bound state via coupling to a repulsive state, as well as (2) quantifying relative dissociation rates at different energies within the same electronic state and between different electronic states.

4.2 Future Directions

Imaging photodissociation of larger metal-containing ions is the main thrust of this project going forward. Moving from \(\text{MX}^+\) to \(\text{ML}^+\) where \(\text{L}\) is a polyatomic ligand can move the focus of these studies from the starting materials to the intermediates and products of model reactions for C-H and C-C bond activation: \(\text{MCH}_2^+\) and \(\text{MCH}_3^+\). The bond energies of most first-row transition \(\text{MCH}_2^+\) and \(\text{MCH}_3^+\) are not known to chemical accuracy of \(\pm 4 \text{ kJ/mol}\), and the majority have only been measured by guided ion beam ion-molecule reactions. Imaging close to the bond dissociation threshold for ground state products with low KER will give a very high precision measurement of the bond energy and should improve on the uncertainties of many existing measurements from ion-molecule reactions by two-fold or more.

Provided imaging is possible close to the threshold of either electronic ground state or excited state alkyl products, the vibrational states of the alkyl fragment should also be
able to be resolved. The best candidates for optimal resolution are those with \( M^+ \) whose ground and first excited atomic energy levels are spaced by more than the vibrational spacing of the highest energy vibrational mode in the alkyl fragment (C-H stretch, \( \sim 3000 \text{ cm}^{-1} \)). This is the case for \( M^+ = \text{Cr, Mn, Cu and Zn} \). The lowest frequency of the three vibrational modes of \( \text{CH}_2 \) gives states separated by \( \sim 1400 \text{ cm}^{-1} \); the kinematics of \( \text{MCH}_2^+ \) are similar to those of \( \text{NiO}^+ \), where the resolution was limited to \( \sim 900 \text{ cm}^{-1} \). Favorability of vibrational levels may also depend on the symmetry of the parent ion in \( \text{MCH}_2^+ \) (\( C_{2v} \) for \( M=\text{V-Zn} \) or \( C_\text{s} \) for \( M=\text{Sc, Ti} \)). There are six vibrational modes of \( \text{CH}_3 \), the lowest frequency of which (the ‘umbrella’) gives a spacing of \( \sim 600 \text{ cm}^{-1} \). Resolving the vibrational levels in \( \text{CH}_3 \) fragments will therefore be close to the limit of this instrument’s capabilities but represents a useful intermediate test case between the resolved spin-orbit levels of \( \text{Ni}^+ \) (\( \sim 900 \text{ cm}^{-1} \)) and the unresolved levels of \( \text{O} \) (\( \sim 200 \text{ cm}^{-1} \)) in the \( \text{NiO}^+ \) studies.

The bond energies of many \( \text{MCCH}^+ \) are also not known to high precision. These molecules additionally have superior kinematics to \( \text{MCH}_2^+ \) and \( \text{MCH}_3^+ \) for imaging experiments, as the neutral co-fragment is almost twice as massive. It has been demonstrated that the imaging instrument can resolve spin-orbit levels in the products, as fine as \( 400 \text{ cm}^{-1} \) in the case of sulfur spin-orbit levels in \( \text{NiS}^+ \) (which has much better kinematics than \( \text{NiO}^+ \)). With similar kinematics, \( \text{MCCH}^+ \) should dissociate to products with clearly defined KER peaks corresponding to the vibrational states of \( \text{CCH}^+ \), as the alkyl product’s low frequency modes such as bending vibrations are separated by at least twice the spacing of the sulfur spin-orbit levels. In addition, \( M^+ \)-alkyl species may form products with resolvable electronic states; some of these candidates may exhibit interesting competition between spin–allowed and – forbidden pathways.
Moving from half-collisions (photodissociation) to full collisions (ion-molecule), KER-initiated reaction studies could put to full use the energy accounting capabilities of photofragment imaging. This molecular orientation- and location of impact-specific experiment would entail forming an [L-M\(^+\)-X] complex, where L is a small molecule ligand (preferably one with high mass and small size, such as CHI\(_3\), in order to maximize collision energy), then photolyzing the M\(^+\)-X bond. A well-defined kinetic energy is imparted to M\(^+\), which, if sufficient to overcome the activation barrier, initiates an M\(^+\)-L reaction. This can lead to reaction pathways that depend on both the energetics (relationship between photon energy and resulting M\(^+\) KER) and dynamics (photon energy dependence of the populated M\(^+\) quantum states) of the MX\(^+\) system. Since the orientation factor and impact parameter are fixed for linear complexes, this experiment would not carry with it the uncertainties that arise from the variable values of these parameters obtained from ion-molecule reactions. Instead, using a known KER-photon energy relationship, one can make measurements based solely upon the kinetic and electronic contributions to the M\(^+\)-L reaction.

Finally, the identification of REPD in photodissociation of MgI\(^+\) by imaging in Chapter 3 might propel imaging studies on systems where it has been suspected to occur by photodissociation spectroscopy. Examples of these include metal cation - water complexes Mg\(^+(\text{H}_2\text{O})\), Ca\(^+(\text{H}_2\text{O})\) and Mn\(^+(\text{H}_2\text{O})\). Each of these systems absorbs and photodissociates in the UV, and it is suspected that the lower than predicted photodissociation yield is due to REPD. Imaging the M\(^+\) photofragments formed over a series of photon energies corresponding to transitions in the reported photodissociation
spectra of M+(H₂O) complexes would reveal to what extent two-photon processes contribute to the signal.

Overall, future studies may focus on measuring the energetics and mechanistic details of known photochemical pathways in M⁺-L species. However, as illustrated in this work for smaller systems, they could also uncover the occurrence of new and unexpected ones. By keeping an eye out for these ‘exceptions to the rule,’ researchers performing the next set of experiments on the imaging instrument might obtain more critical insights into the physical chemistry of elements below the second row of the periodic table.


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