



Dynamics and kinetics of ion-molecule gas phase reactions: Investigations of model systems relevant for catalysis

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"Ich weiß, dass ich nichts weiß." Apologie des Sokrates

Abstract

The present thesis deals with investigations on ion-molecule reactions in the gas phase. Dynamics and kinetics of model systems for catalysis should be studied. Two different experimental setups were used: A modified electrospray ionization mass spectrometer and a 3D velocity map imaging spectrometer. The mass spectrometer was used to investigate transition metal complexes of the type $[M(dgpy)_2](X)_n$ (M = V - Ni) as model systems for (catalytic) gas phase reactions. Structural characterization of the ionic species were performed, including electron transfer dissociation, collision induced dissociation, ultraviolet photodissociation and infrared multiphoton dissociation experiments. In that way, several different ionic species could be assigned, and evidence for reduction of ligand moieties was found. Finally ion-molecule reactions were measured using a self-built gas mixing and inlet system. These were proof-of-principalexperiments for the modification built in this work, and more important first steps for further kinetic investigations. It was shown that Mn^{III}, Mn^{IV} and Fe^{III} react readily towards NEt₃ in the gas phase. By combining the gas phase ion molecule reactions and the UV/Vis laser setup, reactions of the electronically excited Co^{III} complex could be observed as well.

In imaging experiments, the dynamics of the oxygen atom transfer reaction of transition metal cations and CO_2 was investigated. In this work, the focus is on the reaction of the niobium cation Nb⁺. Results are compared to earlier studies with the tantalum cation. Angle and energy differential cross sections were measured at two collision energies. An isotropic scattering around the center of mass with a slight trend towards the forwards hemisphere, which is interpreted as a sign for an indirect mechanism, was observed even at higher collision energies. More energy in the system does not result in much more translational energy of the products. Therefore, it must be partitioned into internal degrees of freedom of the products. Prior to this work it was already known, that a two state reactivity is the main pathway for this reaction. The intersystem crossing along the energy surfaces was found to be the bottle neck. The reaction is trapped in the pre-reaction well, which acts as the rate limiting step.

Both methods show how reactions of model systems can be investigated from different perspectives, providing information about kinetics and dynamics, respectively.

Kurzzusammenfassung

Die vorliegende Arbeit befasst sich mit Untersuchungen von Ion-Molekül Reaktionen in der Gasphase. Dynamik und Kinetik von Modellsystemen für die Katalyse sollen erforscht werden. Zwei unterschiedliche experimentelle Aufbauten wurden genutzt: Ein modifiziertes Elektrosprayionisationsmassenspektrometer und ein 3D velocity map imaging Spektrometer. Mit dem Massenspektrometer wurden Übergangsmetallkomplexe des Typs $[M(dgpy)_2](X)_n$ (M = V - Ni) als Modellsysteme für (katalytische) Gasphasenreaktionen untersucht. Strukturelle Charakterisierung der ionischen Spezies wurden mit Elektronentransferdissoziation, stoßinduzierter Dissoziation, ultraviolet Photodissoziation und infrarot Multiphotonendissoziation durchgeführt. Mehrere ionische Spezies konnten zugeordnet und Hinweise auf reduzierte Ligandenspezies beobachtet werden. Schließlich wurden Ion-Molekül Reaktionen mit Hilfe eines selbstgebauten Gasmisch- und -einlasssystems gemessen. Dies war ein konzeptioneller Funktionsnachweis der Modifizierung, welche in dieser Arbeit gebaut wurde und, noch wichtiger, es waren die ersten Schritte hin zu weiteren kinetischen Untersuchungen. Es konnte gezeigt werden, dass Mn^{III}, Mn^{IV} und Fe^{III} bereits mit NEt₃ reagieren. Durch Kombination der gasphasen Ion-Molekül Reaktionen und des UV/Vis Laseraufbaus, konnten zudem Reaktionen des elektronisch angeregten Co^{III} Komplexes beobachtet werden.

Mit den Imaging Experimenten sollte die Dynamik der Sauerstoff Transfer Reaktion von Übergangsmetallkationen und CO₂ untersucht werden. In dieser Arbeit liegt der Fokus auf der Reaktion des Niobkations Nb⁺. Die Ergebnisse wurden mit denen des Tantalkations aus früheren Studien verglichen. Winkel- und Energiedifferentielle Querschnitte wurden bei zwei Stoßenergien aufgenommen. Eine isotrope Verteilung um den Massenschwerpunkt, mit einem leichten Trend hin zur Vorwärtshemisphere, was als Zeichen für eine indirekte Reaktion interpretiert wurde, wurde sogar für die höhere Stoßenergie beobachtet. Mehr Energie im System resultiert nicht in wesentlich mehr Bewegungsenergie der Produkte. Daher muss diese Energie auf interne Freiheitsgrade der Produkte umverteilt werden. Schon vor dieser Arbeit war bekannt, dass eine *two state reactivity* als wichtigster Pfad für diese Reaktion vorliegt. Das *intersystem crossing* zwischen den Energiehyperflächen wurde als *bottle neck* identifiziert. Die Reaktion ist im Minimum vor der Reaktion gefangen, was als Rate bestimmender Schritt fungiert.

Beide Methoden zeigen, dass die Untersuchung von Reaktionen von Modellsystemen von verschiedenen Perspektiven aus möglich ist und dabei Informationen zur Kinetik oder zur Dynamik erhalten werden können.

Contents

Abstract

Structure of the work

2	Experimental Methods			17
	2.1	Electrospray ionization mass spectrometry		
		2.1.1	General setup of the mass spectrometer	17
		2.1.2	Collision induced dissociation	18
		2.1.3	Electron transfer dissociation	21
		2.1.4	Ion-molecule reactions in the ESI-MS	22
		2.1.5	Infrared multiphoton dissociation	25
		2.1.6	Ultraviolet photodissociation	26
2.2 Crossed beam ion-molecule velocity map imaging		ed beam ion-molecule velocity map imaging	28	
		2.2.1	Ion source chamber	28
		2.2.2	Neutral beam chamber	29
		2.2.3	Velocity map imaging	30
3 Mass spectrometry based investigations on complexes of the type M(dqp), 34	
3.1 Gas-Phase Characterization of Redox-Active Manganese Complex				/ -
	3.1	Gas-P	hase Characterization of Redox-Active Manganese Complexes	34
	3.1 3.2	Gas-P Additio	hase Characterization of Redox-Active Manganese Complexes . onal investigations on complexes of the type M(dgpy) ₂	34 57
	3.1 3.2	Gas-P Additio 3.2.1	hase Characterization of Redox-Active Manganese Complexes . onal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments	34 57 58
	3.1 3.2	Gas-P Additio 3.2.1 3.2.2	Thase Characterization of Redox-Active Manganese Complexes . In the type M(dgpy) ₂ Mass spectra and ETD experiments	34 57 58 63
	3.1 3.2	Gas-P Additio 3.2.1 3.2.2 3.2.3	Thase Characterization of Redox-Active Manganese Complexes . onal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments	34 57 58 63 75
	3.1 3.2	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4	whase Characterization of Redox-Active Manganese Complexes bonal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions	34 57 58 63 75 81
	3.13.23.3	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future	whase Characterization of Redox-Active Manganese Complexes conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions e directions	34 57 58 63 75 81 83
	3.13.23.3	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future 3.3.1	whase Characterization of Redox-Active Manganese Complexes conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions e directions Calibration of the neutral gas density	34 57 58 63 75 81 83 83
	3.13.23.3	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future 3.3.1 3.3.2	whase Characterization of Redox-Active Manganese Complexes conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions e directions Calibration of the neutral gas density IRMPD measurements at FELIX	34 57 58 63 75 81 83 83 83
	3.13.23.3	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future 3.3.1 3.3.2 3.3.3	whase Characterization of Redox-Active Manganese Complexes conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions e directions Calibration of the neutral gas density IRMPD measurements at FELIX Electronically excited state ion-molecule reactions	34 57 58 63 75 81 83 83 83 85 89
4	3.13.23.3The	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future 3.3.1 3.3.2 3.3.3 oxyge	whase Characterization of Redox-Active Manganese Complexes conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments Collision induced dissociation ultraviolet photodissociation Ion-molecule reactions e directions Calibration of the neutral gas density IRMPD measurements at FELIX Electronically excited state ion-molecule reactions	34 57 58 63 75 81 83 83 83 85 89 91
4	 3.1 3.2 3.3 The 4.1 	Gas-P Additio 3.2.1 3.2.2 3.2.3 3.2.4 Future 3.3.1 3.3.2 3.3.3 oxyge Ta ⁺ ar	chase Characterization of Redox-Active Manganese Complexes . conal investigations on complexes of the type M(dgpy) ₂ Mass spectra and ETD experiments	34 57 58 63 75 81 83 83 83 85 89 91 91

1

5	Conclusion					
6	Lite	rature	119			
7	7 Appendix					
	7.1	Mass spectra	131			
	7.2	CID curves	136			
	7.3	UVPD measurements	139			
	7.4	IRMPD measurements	147			

List of Publications

List of conference contributions

List of student projects co-supervised by myself

Curriculum vitae

Danksagung

List of abbreviations

3D	3 dimensional
bру	2,2'-bipyridin
CID	collision induced dissociation
Ср	cyclopentadienyl
CV	cyclic voltammetry
DCS	differential cross section
DFT	density functional theory
dgpy	2,6-diguanidylpyridin
dgpz	2,6-diguanidylpyrazin
e.g.	example given
El	electron impact
ESI	electrospray ionization
ESI-MS	electrospay ionization mass spectrometer
et al.	et alii
ETD	electron transfer dissociation
FELIX	free-electron lasers for infrared experiments
FT-ICR	fourier transform ion cyclotron resonance
GIB	guided ion beam
i.e.	id est
ICR	ion cyclotron resonance
IR	infrared
IRMPD	infrared multi-photon dissociation
ISC	intersystem crossing
IVR	internal vibration relaxation
L	ligand
LVAP	laser vaporization
m/z	mass-to-charge ratio
MCP	micro channel plate
MeCN	acetonitrile
MFC	mass flow controller
MS	mass spectrometer
Nd:YAG	neodymium-doped yttrium aluminum garnet
NEt ₃	triethylamine
OAT	oxygen atom transfer

OPO	optical parametric oscillator
OTf ⁻	triflate
PAHs	polycyclic aromatic hydrocarbons
PD	photodissociation
PES	photo electron spectroscopy
phtmeimb	[phenyl(tris(3-methylimidazolin-2-ylidene))borate]
PID	proportional integral derivative
PMT	photomultiplier tube
рру	2-phenylpyridine
QCT	quasi classical trajectories
R2PI	resonant two photon ionization
REMPI	resonance enhanced multiphoton ionization
RF	radio frequency
SI	supplementary information
SIFT	selected-ion flow-tube
TFY	total fragment yield
TOF-MS	time of flight mass spectrometer
TTL	transistor-transistor logic
UHV	ultra high vacuum
UV/Vis	ultraviolet and visible
UVPD	ultraviolet photodissociation
VMI	velocity map imaging

Control of chemical reactions is utilized all over the world to create new materials and substances used in daily life. [1] These can reach from novel polymers with enhanced properties (e.g., biodegradable material or improved thermal or mechanical stability) over high energy chemicals like petroleum or methanol to fertilizer synthesis or pesticide degradation used in agriculture, just to name a few examples. [2–8] Most of these chemical transformations are made possible by catalysts. Catalysts are often seen simply as an accelerator for a reaction, but in fact they can be so much more. Typically the way a catalyst changes a specific reaction is described by opening of another reaction pathway, starting at the same reactants, going over several transition states and intermediates with a lower activation barrier than the one associated to the original pathway. Thus, the initial energy the reaction needs to start is reduced and the product formation is accelerated (comp. Figure 1). But in fact, rational catalyst design offers the possibility of optimizing a novel reaction pathway, allowing for completely different reaction routes, optimizing the atom economy or resulting in formerly not available products, while always showing a high selectivity towards the desired product. [9–11] One special type of catalytic reactions, are photo-induced catalytic reactions, where the energy of light is utilized to start or drive a reaction. Probably the most well known photocatalytic reaction is done by nature, which is the photosynthesis. Even though, lots of studies have been carried out for over 100 years and still are done today, here, a brief summary of the common knowledge about photosynthesis is given. It transforms the low-energy molecules carbon dioxide and water to carbohydrates and oxygen which have a higher chemical potential. This reaction is driven by the conversion of light energy. [12–14] With this reaction in mind, motivation for research and development in the area of photocatalysis is given. For example found Honda et al. that a self-built electrochemical cell with a TiO₂ electrode and a platinum electrode made the oxygen evolution reaction at the TiO₂ electrode and the hydrogen evolution at the platinum electrode possible, when irradiating the TiO₂ with light. [15]

Scientists all over the world try to find new catalysts that offer new reaction routes, are cheaper in synthesis or live longer before catalyst deactivation. [17–19] One possible approach is to take an existing catalyst and synthesize a similar, new one and then test it for its properties and catalytic capabilities. Another approach is to first investigate existing catalysts as a basis for rational design of new one. This is a valid method because even though a lot of investigation in the field of catalysts is already done, there are many catalytic reactions that are not fully understood yet. [20–22] An important as-



Figure 1: Typical illustration of the way a catalyst changes the pathway of a reaction by utilizing another path, often with several transition states (TS) and intermediates with a lower lying activation barrier than the reaction without a catalyst. [16]

pect of catalysts is their structure, whether electronic structure or geometry. This kind of information is readily accessible via use of a broad range of spectroscopic methods. For example, infrared (IR) spectroscopy offers the possibility to get information about (ro-)vibrational transitions in molecules and from surfaces, thus, revealing their geometry or composition. These can be crucial factors to know about catalysts to disentangle their reactivity. [23] Via spectroscopic investigation in the ultraviolet and visible (UV/Vis) range, the electronic structure of a catalysts orbitals relevant for their chemical reactivity can be probed directly. Additionally it is possible to monitor changes during (catalytic) reactions by time dependent measurements. [24, 25] Furthermore, catalytic reactions are often directly investigated by performing these reactions at small scale in a laboratory. Depending on different factors like the reaction time, temperature, concentrations of reagents or catalyst, solvent or additives used and so on, usually product distribution, yields or rates are measured. [26]

This list could be continued on for a while, but most of these measurements have one thing in common: They are carried out in condensed phase, e.g., in solution, single crystal, on surface or with bulk material. An advantage in condensed phase is, that these measurements often can be done under ambient conditions, close to the *real-life* conditions present during the application. Additionally, results are readily accessible and can be gathered relatively fast. But from the aspect of fundamental gain

of information, this type of experiments always are influenced by more factors than just the catalytic molecules of interest. These influences reach from solvent effects over ion-ion pairing in solution over to inhomogeneous distributions on surfaces or in bulk materials. Further challenges are concerning the sensitivity for the typically reactive transient species. Since catalytic reactions usually consist of multiple elementary steps, it should also be important to investigate all of these on their own.

Here gas phase chemistry comes into play. In gas phase experiments it is possible to investigate single molecules or ions with respect to their intrinsic properties, excluding any influences an experiment in condensed phase always comes along with. In addition it is often possible to investigate site-, state- or energy specific reactions, excluding any impurities or side reactions. [27,28] Depending on the experiment another crucial advantage is the possibility to trap reactive states of a molecule or a reaction, like a transition state or an intermediate complex of e.g., catalyst and reactant. [29–31]

Experiments in vacuum, i.e., in the gas phase, come along with several problems. There, the detection is the first problem to encounter. In condensed phase, usually measurements are done *directly*, e.g., intensity of light before and after the experiment. Since the particle density in a vacuum is very low, this detection is not sensitive enough. Therefore, other ways of detection are needed and those are based on detector systems that can measure charged particles, i.e., ionic species. This is the case in mass spectrometers, which measure the mass to charge ratio (m/z) of the ions. Relative ion intensities before and and after the experiment or fragment appearance and so on are used to get information *indirectly* from the measurements. Regardless whether the ionization takes place before or after the experiment, a high sensitivity and precision is a benefit of gas phase investigations. Thus, mass spectrometers are widely used and various models have been established. [32, 33]

Similar to condensed phase, it is possible to investigate molecules or their reactions in many different ways. It is important that before the experiments the objective of it must be clear, because there are several different aspects to reactivity that cannot all be obtained from the same experiment, respectively experimental setup. Such information could be:

- What is the structure of the molecule in the gas phase?
- Which reaction is a model system able to realize?
- What about the reaction energetics, is it exergonic or endergonic?

- What is the time scale of the reaction?
- What are the different elementary steps along the reactions' pathway?
- How is the the energy partitioning of the products?
- Does a direct or indirect mechanism occur?

These questions address two points about reactions: kinetics and dynamics. The first one is typically about the rates of chemical reactions, while the latter studies on an atomic scale how elementary steps of a reaction take place and how the forces involved effect it.

The first of these questions is answered similar to condensed phase, namely by pairing the properties of gas phase experiments together with the vast possibilities of spectroscopic methods. In this way fundamental, intrinsic properties of model systems can be investigated in a very accurate way. [34, 35] To measure UV/Vis or IR spectra of molecules in the gas phase, advanced methods have to be used, because as already mentioned the particle density is too low for classical absorbance measurements. Thus, a wide variety of methods have been developed over the years, making use of high energy light sources like lasers. A nowadays common approach is the resonance enhanced multiphoton ionization (REMPI) technique, where one laser is used for the excitation and one for the ionization of the molecule. This ionization can occur as simple electron detachment or fragmentation of the molecule. The ionic product is afterwards detected by means of mass spectrometry. In this way new information about the energetics or the structure of small molecules can be obtained. These can be, e.g., the number of absorbed photons and their distribution, as well as fragmentation patterns depending on the laser fluence. [36] Gerhards et al. have published a review to the topic of gas phase spectroscopy, concentrating on structure determination of isolated amino acids and peptides. There, they also describe various methodologies to efficiently create and determine different isomers. [37] Similar results, but with a focus on inorganic compounds, are shown by Fielicke. [38] Insights into binding sites and energies as well as activation barriers for small molecules on transition metal clusters are presented. In the gas phase it is also possible to cool down the investigated molecules to cryogenic temperatures, i.e., around 6 K. With that resolution can be increased since less states are occupied. A further advantage is the possibility of tagging, which means adsorbing unreactive molecules which dissociate with small amounts of absorbed laser energy. This increases the sensitivity of action spectroscopy even further. [39, 40] The

field of gas phase spectroscopy has not only experienced a lot of development of different mass spectrometric experiments, but also the laser systems used got more and more elaborate, such as synchrotron or free electron lasers. [39,41] For making mass spectrometers accessible for lasers, the setup of the experiments are often very elaborate, as well as the pathway for the light and the laser systems. In Figure 2 several setups, with various traps irradiated by different lasers are shown.



Figure 2: Compilation of different setup designs for laser spectroscopy of ionic molecules and clusters in ion traps. Shown are a linear quadrupole trap of a LTQ mass spectrometer coupled with an OPO laser [42] (a), a 3D Paul-trap, modified for laser access [43] (b), a setup with a FT-ICR cell coupled with the IR laser of the free electron laser at FELIX [44] (c) and a cryo cooled FT-ICR cell coupled with an OPO laser system [40] (d).

As the above mentioned experiments already suggest, among gas phase experiments, one can differentiate between two types: ion trap mass spectrometer and experiments with ionic or molecular beams.

For the first one, some sort of ionization source, where the molecules are ionized is mandatory, for example an electron impact (EI), laser vaporization (LVAP) or electrospray ionization (ESI) source. The latter one though, doesn't ionize molecules, but separates them out of a solution from neutral molecules. The other two do ionize usually gaseous molecules or metal atoms, respectively. After the ionization, ion optics (e.g., electrostatic focusing lenses) are used to navigate and select the molecules of interest (e.g., via a quadrupole mass analyzer). At the end the ions get into the part where experiments take place, the ion trap. There are many various traps in different shapes

and functionalities, for example linear hexapole traps, three dimensional quadrupole traps (Paul trap) or Fourier transform ion cyclotron resonance (FT-ICR) cells. There, ions can be stored, depending on the trap for several milliseconds to seconds or even longer. In this time, different experiments can be performed, like action spectroscopy, ion-molecule reactions or fragmentation experiments. [45, 46]

In the case of experiments with beams, two options are possible: Experiments with neutrals by the use of a molecular beam (e.g., by super sonicexpansion of a neutral gas), the sample molecules get ionized during or directly after the experiment. For example the above mentioned REMPI experiment, or creation of ions with an ion source, followed by taking up these ions in a stream of an inert gas like helium are established methods. These beams are then often crossed by another beam, whether laser, molecule or ion beam, depending on the subject of the study, also speaking of crossed beam experiments. [47, 48]

Both types offer different possibilities, advantages and disadvantages. Within an ion trap, usually higher densities are applicable, which can lead to collisional cooling or thermalization during the experiments. This is also referred to as multi-collision conditions. This enables energy distribution, both inter- and intramolecular into different degrees of freedom resulting in a thermal distribution, series of reactions or simply higher intensities for spectroscopic measurements. Crossed beam experiments on the other site usually are operated under so called single-collision conditions, which are achieved by a lower pressure and short interaction times. Since no collisions with a surrounding medium takes place, a decoupling of temperatures or occupation of different degrees of freedom is observed. Therefore, the energy in the systems plays a crucial role.

Depending on the subject of a specific study, these are important facts to consider. In the following, this will be shown on some examples.

The first example is about the catalytic formation of HCN on a platinum surface and different studies on similar model systems, providing answers to different question (kinetics and dynamics). In that manner, Hasenberg et al. studied reaction rates of the reaction (1) on Rh and Pt surfaces respectively. [49, 50] Their experiment consisted of two separate chambers, one steady-state flow reactor where the reaction was performed and one analysis chamber equipped with an Auger electron spectroscope and a mass spectrometer, both at ultra high vacuum (UHV). With this setup, they were able to determine the reaction rates, activation energies and surface coverage at different temperatures and achieved well agreement with the Langmuir-Hinshelwood model.

$$NH_3 + CH_4 \longrightarrow HCN + 3H_2$$
(1)

Further investigations of Aschi et al. were carried out a few years later. [51] They used a Fourier transform ion cyclotron resonance mass spectrometer to measure the same reaction but with atomar Pt⁺ ions instead of a metal surface. Their measurements allowed them to propose two reaction sequences how the HCN molecule is formed: One over the formation of an intermediate ionic species without platinum (eq. (2)) and another one with a complex intermediate of the type [Pt, C, N, H₃]⁺ (eq. (3)), whereas both sequences have the precursor ion [PtCH₂]⁺ in common.

$$[PtCH_2]^+ + NH_3 \longrightarrow CH_2NH_2^+ + [PtH]$$
⁽²⁾

$$[PtCH_2]^+ + NH_3 \longrightarrow [Pt, C, N, H_3]^+ + H_2$$
(3)

Other than just the intermediates and with that the proposed reaction routes, they also were able to measure the reaction rates for the formation of the intermediates.

Another reaction investigated extensively in literature is given in equations (4) and (5).

$$Fe^+ + C_3H_8 \longrightarrow FeC_3H_6^+ + H_2$$
(4)

$$Fe^{+} + C_{3}H_{8} \longrightarrow FeC_{2}H_{4}^{+} + CH_{4}$$
(5)

Byrd et al. measured the reactions of Fe^+ with different alkanes, including the above mentioned reaction. They used an ICR cell mass spectrometer and infused the gaseous alkanes into the cell with the isolated iron cations. In this way they were able to record the different reaction products and their specific abundances. [52] They were able to conclude about the nature of the ionic and the neutral reaction products, but couldn't quantify the reaction rates.

Experiments like this are examples for measurements under single-collision conditions. Thus, by a high vacuum and short interaction times, no or just a few collision with each other, reactants or background particles happen. Therefore, no energy dissipation takes place, but it is preserved in the reactants. Single steps along a reaction pathway can then be investigated in more detail, revealing information about dynamics, like state transitions, elementary steps or energy partitioning. [53, 54] In contrast

to that are multi-collision conditions. This means, that the pressure where the reaction takes place is high enough for ions and neutral reactive gas atoms or molecules having multiple collisions that could lead to a reaction before the detection step. Furthermore, a buffer gas is typically present so that energy dissipation into the environment takes place before and after reactions. In experiments with multi-collision conditions usually kinetics like rates and energetics of a whole reaction are measured as quantitative values in addition to qualitative information like product distribution or relative differences in similar reactions. [55–57] Speaking of quantitative observations like reaction rates, one has to differentiate between different rate constants and cross sections (compare Figure 3). The rate constant k(T) refers to the thermal rate constant only depending on the temperature of the system where the reaction takes place. This is the rate that is usually measured in most condensed phase kinetic experiments. Alternatively it can be measured for gas phase reactions under multi-collision conditions because thermalization of the system is possible. An example for this are experiments using the flowing-afterglow technique like Bierbaum et al. showed. [58] They measured the reactions of N_2H^+ , N_4^+ or N_3^+ with water vapor, finding three different reactions, and measuring the products as well as the thermal rate constants k(T). Also Gronert and Parchomyk et al. measured thermal rate constants but in ion trap experiments. [59,60] Therefore, they had to modify the mass spectrometers in their laboratories to insert neutral gas into the trap. The difficulty here is the density of the neutral gas introduced into the trap, because the actual pressure inside a trap is not a readily accessible value or at least only with a relatively high error (ca. 30% for typical vacuum meters). They measured literature known reactions under different conditions and from comparison with known values they could derive effective temperatures or rate constants for the reactions inside the trap respectively. Another type for measuring k(T) for gas phase reactions is shown by Viggiano et al. With a various temperature selected-ion flowtube (VT-SIFT), they are able to measure reaction rates for gas phase ion-molecule reactions accurately at different kinetic energies and temperatures over a range of 85 -500 K (see example reactions (6) and (7)). [61,62]

$$Ar^{+} + HCl \longrightarrow HCl^{+} + Ar$$
(6)

$$FeO^+ + H_2 \longrightarrow Fe^+ + H_2O$$
 (7)

Although Byrd et al. didn't measure reaction rates, their results about the observed reaction products were further used by other groups. Armentrout et al. measured



Figure 3: Overview of different rate constants (*k*) and cross sections (σ) in dependency of different physical quantities (quantum states *n*, *n'*, scattering angle θ , relative velocity v_{rel} or temperature *T*) and how they are linked to each other. The "Energy dependent state-to-state differential cross section" would be the one with the most precise information, but is hardly accessible with up to date known methods. The "Thermal rate constant" instead is the macroscopic quantity that is usually measured in the most experiments, especially in condensed phase.(adapted from [63])

specifically these two simultaneously occurring reactions with a guided ion beam (GIB) mass spectrometer. [64] The important part about this experiment is simply but vividly described in an earlier work: "a beam of ions of known mass and well-defined kinetic energy is allowed to react with neutral molecules under single-collision conditions". [65] With this setup, equipped with two different ion sources, they could measure state-specific cross sections of the $Fe^+({}^6D)$ and $Fe^+({}^4F)$ states and show a nonadiabatic behavior. With resonant two photon ionization (R2PI) of metal atoms, combined with photoelectron spectroscopy (PES) Hanton et al. were able to create Fe^+ ions in well-characterized state distributions. They crossed the beam of these iron ions with a molecular beam of propane in an interaction section and measured ionic products via a time-of-flight mass spectrometer (TOF-MS) in a typical Wiley-McLaren arrangement. [66, 67] With this laser spectroscopy based setup they were able to measure state-specific cross sections for the above mentioned reactions (4) and (5) again, but with even more detail concerning the *J* levels of the Fe⁺ states at the given collision

energy of 0.22 eV. Their results showed a higher reactivity for J = 5/2 than for J = 9/2and J = 7/2 within the Fe⁺(⁴F) state. The experiment above is an example for a crossed beam experiment, where a beam of ions and another beam of neutral molecules are crossed or overlapped, spatially and temporally, to observe ion-molecule reaction. Crossed beam experiments are conducted under single-collision conditions and both beams can be well controlled concerning velocity and internal energy, as already can be seen in the before described example. With this type of experiment and the control of the internal energy and velocity of the ions and molecules, not reaction rates but rather cross sections can be measured. An advancement to the ion imaging experiments, is the development of the velocity map imaging (VMI) technique. The most important difference is the product ion detection. Instead of a Wiley-McLaren time-offlight mass analyzer the acceleration electrodes are used with different voltages and the grid was omitted. This change was first brought up by Eppink and Parker. [68,69] In this way some resolution in mass-to-charge ratio is lost, but it is possible to focus ions of the same velocity onto the same spot of the detector. This results in an imaging of the velocity distribution and with some advancements also giving information about the angle distribution over 4π . [70–72] One of the first reactions studied with this VMI technique, is similar to reactions (4) and (5), but with Co⁺ instead of Fe⁺ (see (8) and (9)).

$$Co^+ + C_3 H_8 \longrightarrow CoC_3 H_6^+ + H_2$$
(8)

$$Co^{+} + C_{3}H_{8} \longrightarrow CoC_{2}H_{4}^{+} + CH_{4}$$
(9)

The group of Weisshaar expanded their existing experiment by the imaging electrodes and the associated detector system. In that way, they still were able to create state specific ions and a neutral beam of controlled velocity. [73] After the reaction, the product ions are accelerated perpendicular and the distribution in velocity vectors (translational energy) and angles is measured for each ionic product individually, giving differential cross sections (DCS). They could show that reaction (8) doesn't have an exit channel barrier, while they could propose a well in the energy surface where $Co^+(C_2H_4)(CH_4)$ survives for a short time and afterwards decays statistically. [74]

Also other experiments showed the strength of the VMI technique to measure DCS. Like Wester et al. and Meyer et al. showed, it is possible to describe many different ion molecule reactions in this way. They could provide precise information about the dynamics of various reactions. Usually these measurements are complemented by

high level theoretical works, which facilitate interpretation of the experimental results. On the other hand, theory also profits from these complementary works. Theoretical results can be compared to real experimental data, resulting in a bench marking for the novel methods. [75–77]

Typically the systems studied with VMI are only a few atoms in size, like in (8) and (9) there are 12 atoms involved. One explanation for this small size is the computational effort, when it comes to theoretical work supplementing the experimental data. The bigger the systems are, the more complicated they are to calculate. Another reason is that the more atoms a system consists of, the more degrees of freedom there are where the energy can be partitioned into. This makes the interpretation of the experimental data more complicated too. Finally, it should be mentioned, that since this is a relatively new technique, first the smallest systems should be understood before increasing the size of the model systems.

These examples, as well as the before mentioned ones, show how the improvement of different techniques can provide different levels of information, from which the later experiments can benefit. The variety in experiments is also described and how they can be used each for their own specific question or subject of investigation. Both, kinetics and dynamics can be studied very precisely already. Combining those two areas, i. e. the results from different experiments can provide different perspectives of the same reactions. This helps to understand a whole reaction as precisely as possible. With this in mind it is reasonably to look forward towards further improvement of experimental setups to answer new questions or obtain more detailed information over different (catalytic) systems and their models.

Structure of this thesis

This work is divided into two main parts, one related to structure and kinetics of a photocatalyst and one related to a model for transition metal chemistry. In the first one different mass spectrometric investigations of six complexes synthesized in the group of Katja Heinze (JGU Mainz) are conducted. This complex chemistry based topic covers specifically the points of catalyst studies motivated in the introduction and the question of intrinsic properties of the catalyst molecules itself, by measuring gas phase stabilities and absorption spectra in gas phase. Furthermore, the questions about reactivity should be addressed and therefore it was mandatory to establish an extension to an existing commercial ion trap mass spectrometer, making it possible

to qualitatively (product distribution, relative reaction kinetics), and in the end quantitatively (k(T)) measure gas phase ion-molecule reactions. To further encourage the reader to this topic, a short, specific introduction into these complexes is given:

Transition metal ions and their complexes can cover a big range of redox potentials, depending on oxidation state and ligand environment. As only one example, East et al. show nine complexes from literature, all with a manganese(IV) central ion and a [MnN₆] coordination with a range in their oxidation potential from $E_{1/2} = -1.48$ to +1.69 V vs ferrocene (compare Figure 4). [78]



Figure 4: Compilation of manganese(IV) complexes with their respective potentials for the $Mn^{IV/III}$ redox step.(Figure taken from literature [78])

Next to this, there are some complexes known, that exhibit even higher redox potentials when excited by light, e.g., $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)]^+$ ($E_{1/2}^* = 1.30$ V), [79] $[Fe(phtmeimb)_2]^+$ ($E_{1/2}^* = 1.0$ V), [80] and $[Co(dgpz)_2]^{3+}$ ($E_{1/2}^* = 2.37$ V) [81] (all values vs ferrocene). Given this rich redox chemistry of transition metal complexes, in the

groups of Katja Heinze and Eli Zysman-Colman a series of 3d metal complexes was synthesized with the ligand 2,6-diguanidylpyridine (dgpy), which is a tridentate chelate ligand offering push and pull properties thus able to stabilize the complexes in several oxidation states and always octahedral geometry. The metal ions of which the complexes were synthesized are V³⁺, Cr³⁺, Mn^{4+/3+/2+}, Fe^{3+/2+}, Co³⁺, and Ni²⁺ (compare Figure 5). [78,81–84] Among these complexes, manganese(IV) and cobalt(III) showed a strongly increased redox potential in the excited state ($E_{1/2}^* = 2.0$ V and $E_{1/2}^* = 1.85$ V respectively). For manganese a strong oxidative capability could be shown in a reaction with benzene or acetonitrile, while the cobalt complex was used for a photocatalized trifluoromethylation of PAHs. [81] Even though for the other complexes such redox potentials and oxidation reactions were not yet observed, they still show interesting absorption properties like a panchromatic absorption in the UV/Vis range. While all studies with the complexes mentioned above were carried out in condensed phase, here, results of complementary gas phase investigations will be shown.



Figure 5: Schematic drawings of the complexes $[V(dgpy)_2]^{3+}$, $[Cr(dgpy)_2]^{3+}$, $[Mn(dgpy)_2]^{n+}$, $[Fe(dgpy)_2]^{2+/3+}$, $[Co(dgpy)_2]^{3+}$ and $[Ni(dgpy)_2]^{2+}$. All complexes have the two 2,6-diguanidylpyridine ligands and thus the octahedral geometry in common. [78,81,83,84]

The second topic of this work is all about crossed beam 3D velocity map imaging. In the group of Roland Wester (university Innsbruck), a new VMI spectrometer was built,

equipped with a laser vaporization source to create metal ions. [85] The whole experiment was then moved to Kaiserslautern and after setting it up again, the first reaction investigated was the oxygen atom transfer (OAT) reaction between the tantalum cation Ta⁺ and CO₂ (10). [86]

$$Ta^{+} + CO_{2} \longrightarrow TaO^{+} + CO$$
⁽¹⁰⁾

In literature a huge interest exists for this reaction. Firstly, it is about the activation of carbon dioxide, which is especially nowadays a very important topic. On the other side it is a model reaction for which already products and reaction rates as well as energetics were measured [87, 88]. In the work of Meta et al. angle- and energy-differential cross sections were measured at three collision energies for the first time. While at low energies the product ions are mainly isotropically scattered around the center of mass, at higher energies a slight forward trend was visible (compare Figure 6). On the basis of the comparison of internal and kinetic energy distribution, the formerly known multistate reactivity was further investigated. [89] Target was to find out where exactly the intersystem crossing (ISC) happens and what is the rate determining step in this reaction. First assumptions for these questions could be made, but not finally answered. Interestingly, even for high collision energies, signs for a indirect reaction mechanism were observed.

In this work, the complementary reaction with the niobium cation Nb⁺ was investigated (chapter 4). The target of these experiments was to obtain further understanding about the reactions of metal cations towards CO_2 in an oxygen atom transfer reaction (OAT). For this reason angle- and energy differential cross sections should be measured for reaction (11).



Figure 6: Results of the first VMI experiments with our setup after it was moved to Kaiserslautern. Shown are the experimental differential cross section (a-c), i.e., the velocity distribution of the product ions TaO⁺ at three collision energies. The graphs d-f show the angular integrated distributions. At low collision energies and scattering angles around $\theta = 180^{\circ}$ residual signal of Ta⁺ can be seen in both types of illustration. A slight asymmetry in forward direction arises at 2.0 eV (c, f). The simplified Newton diagram at the top clarifies forward and backward hemispheres. [86]

From there the following question should be tackled:

- Is the rate determining step the ISC or a submerged transition state?
- How is the energy of the products partitioned?

$$Nb^+ + CO_2 \longrightarrow NbO^+ + CO$$
 (11)

Since the reaction coordinate of tantalum did not show a submerged barrier (Figure 7), it also was not expected for niobium. Anyways, the reaction was known to show a lower efficiency. Therefore, the question was if the ISC is the rate determining step or the reaction of the lighter homologue has a submerged transition state. This was unclear because by going from a 5d transition metal cation towards a 4d cation the spin orbit coupling is weaker and therefore an impact on the ISC should be observed. To tackle this question it was also important to disentangle the energy partitioning in the products.



Figure 7: Reaction coordinate of the reaction of $Ta^+ + CO_2$ for quintet, triplet and singlet states. A ISC is suggested between the pre-reaction complex and the quintet transition state. [86]

First a short methods chapter will explain the basics of the present experimental setups and the methods used, then the discussions about the results will follow, concluded by a summary that brings everything back together again.

2 Experimental Methods

2.1 Electrospray ionization mass spectrometry

Electrospray ionization mass spectrometry (ESI MS) was first used by Malcolm Dole in 1968. [90] For the further developments in the 1980s, John Fenn was awarded with the Nobel prize. [91, 92] This technique has advanced towards a very powerful tool to transfer ions from solution into gas phase. [93]

ESI is an ambient ionization method that only separates the ions inside a solution from the neutral molecules by use of electrical fields. This is a soft ionization technique, able to transfer a broad range of different ions, from small ions like solvent molecules up to whole viruses with masses over 5 MDa. [94, 95] With this powerful ion source almost all kinds of soluble ions can be investigated, depending on the mass analyzer combined to the ESI source.

2.1.1 General setup of the mass spectrometer

All experiments presented in chapter 3 were carried out on three different amaZon mass spectrometers from Bruker Daltonics: amaZon ETD, amaZon speed, and another amaZon ETD in the FELIX laboratory. Since these three mass spectrometers are very similar (compare Figure 8), their functionalities will be explained just once.

The amaZon mass spectrometer (MS) is equipped with an Apollo II ESI source, where the ions are separated from the solvent. By an electrical field of about 4 kV the ions are guided through the transfer capillary and into the first of the four differential pumped vacuum stages. A dual ion funnel, which is located "off-axis" in relation to the transfer capillary, ensures that no neutral molecules get into the higher vacuum stages. A dual octopole ion guide leads and focuses the ions into the last vacuum stage. Here, the Paul trap is located, where all the experiments take place. [97] It consists of one ring electrode and two end plates with a small hole to let the ions through. On the ring electrode a high voltage RF amplitude is applied, which creates an oscillating quadrupolar electrical field. The end plates are either grounded or an auxiliary voltage (DC or RF) can be applied to stop ions from entering the trap during experiments, extract ions from the trap for an isolation process, lead them onto the detector for the mass scan or accelerate the ions. For efficient trapping of the ions it is important to slow down the arriving ions. This is achieved by a helium buffer gas inside the Paul trap with which the ions collide to thermalize. The pressure inside is held constant in a specific window in the range of 10^{-3} mbar by a proportional integral derivative (PID) gas

2 Experimental Methods



Figure 8: Detailed illustration of the amaZon ETD mass spectrometer. The red line demonstrates the pathway of the ions through the different parts of the mass spectrometer. The ions get separated from the solution at the atmospheric pressure ion source, purified from neutrals at the dual ion funnel with its off-axis geometry and at the fourth vacuum stage into the ion trap. Fluoranthene radical anions are generated at the nCl source. All three used mass spectrometers have the shown parts in common. The amaZon ETD in Nijmegen as well as the amaZon speed are additionally equipped with an optical access into the trap. [96]

controller. The pressure of the gas inside the Paul trap is crucial for the experiments because with a too low pressure ions aren't sufficiently decelerated, resulting in a loss of signal. On the other side, if the pressure is too high, a worse resolution or even decrease of ion intensity can be observed. Additionally, the MS is equipped with an Electron transfer dissociation (ETD) source (see subsection 2.1.3). Two of the mass spectrometers do have holes inside the ring electrode and two mirrors underneath it, to focus a laser through the trap. [43] The following chapters describe the methods used in this work in more detail.

2.1.2 Collision induced dissociation

Collision induced dissociation (CID) is a tandem mass spectrometric method for the characterization of isolated molecules. In the Paul trap this experiment takes place as follows: A package of ions gets trapped, followed by isolation of the ions with the mass-to-charge ratio (m/z) of interest. In the next step an auxiliary RF voltage is applied to
the exit cap, usually with the resonant frequency of the isolated ions. The resulting field excites and thereby accelerates the precursor ions on their trajectory. When the accelerated ions collide with the He atoms inside the trap it is possible that they fragment, depending on the excitation voltage and the binding or dissociation energies. [98] It should be noted that in addition to binding energies, there are usually attractive interactions of the fragments, which hold the fragments together in a loose complex and need to be overcome by the collision energy to separate those fragments. Afterwards all ionic fragment species can be measured. With the Paul trap it is possible to perform MSⁿ experiments, which means subsequent steps of isolation and fragmentation. With this method important information about geometrical structure can be obtained. By increasing the voltage of the excitation amplitude (E_{LAB}) step-wise in V, it is possible to get gradual fragmentation. From the absolute intensities of the precursor ion (I_{abs}^{pre}) and the different observed fragment ions (I_{abs}^{fragi}), the relative intensities (I_{rel}^{pre} for precursor ions, I_{rel}^{fragi} for fragment ions) can be calculated after the following formula:

$$I_{rel}^{pre}(E_{LAB}) = \frac{I_{abs}^{pre}(E_{LAB})}{\sum_{i} I_{abs}^{frag_i}(E_{LAB}) + I_{abs}^{pre}(E_{LAB})}$$
(12)

$$I_{rel}^{frag_i}(E_{LAB}) = \frac{I_{abs}^{frag_i}(E_{LAB})}{\sum_i I_{abs}^{frag_i}(E_{LAB}) + I_{abs}^{pre}(E_{LAB})}$$
(13)

Relative intensities plotted against the excitation amplitude will result in so called CID curves, breakdown curves for the precursor or appearance curves for the fragments (compare Figure 9).

The energy associated to the increased electric field from the excitation amplitude (E_{LAB}) is assumed to be fully converted into kinetic energy of the ions if the frequency is resonant with the m/z ratio of the ions. The amount of energy transferred between ions and He atoms by inelastic collisions depends mostly on the mass ratio of the ion (m_{ion}) and the helium (m_{He}) . [100, 101] Therefore, a center of mass transformation is commonly used as a correction (see eq. (14)).

$$E_{COM} = E_{LAB} \cdot \left(\frac{m_{He}}{m_{He} + m_{ion}}\right) \tag{14}$$

In case of linear acceleration of ions in an electrical field, formula (15) describes the conversion of electrical energy (E_{el}) towards kinetic energy (E_{kin}) , with the elementary charge $e = 1.602 \cdot 10^{-19}$ C, the charge number *z*, the potential difference *U*, the mass *m*, and the velocity *v*.



Figure 9: The graphic shows an example plot of relative abundances of precursor ions (red circles) and fragment ions (black squares), giving CID breakdown or appearance curves respectively. The lines are the sigmoidal fits and the blue circle indicates the point of the $E_{COM}^{50\%}$ value.(adapted from [99])

$$E_{el} = e_z U = \frac{1}{2} m v^2 = E_{kin}$$
(15)

Due to the charge number *z* in this formula, this applies to ions of all charge states. Therefore, CID experiments with ions of different charge states are usually carried out in linear experimental setups. [102] In that way it is possible to measure absolute energies of dissociation barriers with correct calculations of kinetic energies resulting from the electric acceleration field. In case of Paul trap CID experiments the excitation is achieved with an oscillating field and comparable experiments are usually done with ions of the same charge state. In this work, CID experiments with ions of different charge states were carried out, to get qualitative information about the gas phase stability of the ions, relative to each other. Therefore, as an approach for the calculation of the electric energy converted into kinetic energy of ions with different charge states, equation (14) was extended by a linear approximation (see eq. (16)).

$$E_{COMz} = E_{LAB} \cdot \left(\frac{m_{He}}{m_{He} + m_{ion}}\right) \cdot z \tag{16}$$

The resulting value is used without unit and is only utilized as a qualitative value to compare all species with each other, even those with different charge states. A correct quantification of the energies would need to be done for every ion, as well as every excitation frequency individually and would probably only result in a little upset or stretch of the CID curves in a qualitative point of view. The resulting CID curves can be fitted with an sigmoidal fit function, shown in equation (17), giving the $E_{COMz}^{50\%}$ value. This describes the point where 50% of the precursor ions are fragmented and can be used as a qualitative value to compare relative gas phase stability.

$$I_{fit}^{pre}(E_{COMz}) = \frac{A}{1 + e^{-B(E_{COMz} - E_{COMz}^{50\%})}}$$
(17)

2.1.3 Electron transfer dissociation

Electron transfer dissociation (ETD) is a method to reduce or fragment multiply charged cations. All mass spectrometers used in this work are equipped with an ETD source. There, a filament is surrounded by methane gas. The filament then releases electrons which are taken up from the methane molecules. Additionally there is fluoranthene in a small reservoir which takes the excess electron in a second step. Afterwards these fluoranthene radical anions are added into the Paul trap to the already isolated ions. Then they are given a set time to transfer their electron to the cations. The observed products can be just reduced species or fragments of the precursor ion. In that way, it is possible to form reduced species of the ions of interest in gas phase, that eventually aren't accessible directly from solution.



Figure 10: Schematic ETD process. First step is trapping and isolating the multiply charged cations inside the Paul trap (top). Second is transfer of the negative ETD reagent ions (fluranthene) into the trap, leading to ion-ion reactions (bottom). [96]

2.1.4 Ion-molecule reactions in the ESI-MS

Ion-molecule reactions in the gas phase can provide intrinsic information about ions, neutrals, and their reaction with each other without interaction with solvent molecules or ion pairing. [103–105] By ESI-MS often many different ionic species are created from one sample solution and by subsequent isolation inside the Paul trap it is possible to investigate them one after another. The difficult part is the introduction of the neutrals into the trap. In this work, a gas mixing unit in accordance to Parchomyk et al. [60] and Martens et al. [43] and a control system were built to introduce a neutral gas into the Paul trap in a controlled manner.

The gas mixing unit consist of a stainless steel tank (V = 0.5 L), an inlet for a reactive gas, an inlet for a liquid reactant and an inlet for helium. In this way, it is possible to either use a pure reactive gas or seed it into helium by mixing the reactive gas and helium using the tank. For a liquid reactant, when the vapor pressure is high enough, it is also possible to seed it into helium. The pressures of the reactant and the helium are controlled by use of a manometer in direct vicinity of the steel tank.



Figure 11: Schematic drawing of the gas mixing unit (a) and the control section (b). Shown are the two inlets for reactive gases as gas or vapor of a liquid on the left top and bottom respectively. Helium gas can be added via the marked inlet, next to that is the vacuum line to evacuate the system at whole or parts of it. The manometer (PI) shows the pressure of the respective gases inside the piping system and the tank can store the gas mixtures over long time intervals. The final gas mixture is then directed to the next stage "towards control section". The reactive gas coming from the mixing unit is directed through a pressure regulator into the gas controller TGC1 (referred as reactant MFC), that controls the further gas flow. The general valve then gives pulses of gas into the MS, where it can be combined with the helium buffer gas from the "helium MFC". The pulse generator controlling the general valve is not depicted.

The gas mixtures with defined concentrations can be prepared and stored for several days or even weeks before the pressure is too low for further experiments and the tank needs wo be refilled. The whole gas line system, as well as the tank can be evacuated by a turbomolecular pump (compare Figure 11 a). The control section shown in Figure 11 b) is located between the mass spectrometer and the mixing unit.

First the gas mixture passes an in-line pressure regulator, where the pressure can be controlled. Then there is a proportional integral derivative (PID) gas controller (TGC1), which is the same type that is used internally for the helium pressure inside the trap (TGC0). [106] With that, a constant gas flow is achieved, that can be set with the software AtlasControl to a relative value in relation to the maximum possible flow rate, i.e., TGC1 = 10 means TGC1 is 10% opened. After the gas controller a pulsed three-way valve (General valve Series 9, Parker) is located. It is controlled via an lota One controller (Parker), which is a pulse generator that can give electrical pulses to open the general valve. It has four operation modes: An internal one shot mode, where it creates just one pulse for a set amount of time after pressing the start button. Second is an internal cycle mode, where it sends pulses in a set frequency until the user presses the stop button. The other two operation modes, an external one shot and an external cycle mode, are similar but the starting signal now is a TTL pulse from another device, in the present case the MS. The timing of the created gas pulse can be synchronized to the timings of the mass spectrometer. It should be mentioned that the pulse duration (t_{pulse}) can be varied from about 200 μ s to 9999 min, where very long times can be used as continuously introduction of neutral gas into the trap. It should be noted that it takes about 200 μ s to reliably open the valve, which is the reason why no shorter times are possible with the currently installed valve. Therefore, these 200 μ s are a off-set and the valve behaves linear at a higher duration. The created gas pulse can afterwards be mixed with helium and is introduced into the ion trap through the same gas line as the buffer gas helium.

For one experiment, the ions of interest get isolated and afterwards trapped for $t_{\text{trap}} = 0 - 2000 \text{ ms}$, with one setting for the gas flow at TGC1 and one specific duration t_{pulse} . It was found that the ion accumulation step is a good point in the measurement cycle to introduce the gas into the trap, so the gas will arrive, when the trapping time starts. Since we measure reactions, the trapping time also describes the reaction time. For pulsed introduction of neutrals into the trap, it was found that the reaction time should not be longer than 500 ms, since the amount of neutrals inside the trap decreases due to diffusion out of the trap. For continuous mode, t_{trap} has no limitation in that way. For the evaluation of an experiment, the intensities of precursor ions (I_{abs}^{pre}) and the product ions (I_{abs}^{pre}) are used to calculate relative intensities (see eq. (18) and (19)), similar to the CID experiment.

$$I_{rel}^{pre}(t_{trap}) = \frac{I_{abs}^{pre}(t_{trap})}{\sum_{i} I_{abs}^{pro_i}(t_{trap}) + I_{abs}^{pre}(t_{trap})}$$
(18)

$$I_{rel}^{pro_i}(t_{trap}) = \frac{I_{abs}^{pro_i}(t_{trap})}{\sum_i I_{abs}^{pro_i}(t_{trap}) + I_{abs}^{pre}(t_{trap})}$$
(19)

If plotted against the reaction time t_{trap} , a relative reactivity between different ions, different neutrals, or different gas flows can be observed. For quantification a fit depending on the reaction (usually pseudo-first order) has to be done. For this fit it is crucial to know the density of the neutral added into the trap. As for almost all gas phase experiments it is difficult to get precise values for this density. First calibration experiments were carried out as described in chapter 3.3.1, but the results have not been applied to the measurements of this work, yet (chapter 3.2.4).

2.1.5 Infrared multiphoton dissociation

Infrared multiphoton dissociation (IRMPD) is a method for measuring infrared spectra of isolated molecules in the gas phase. It provides similar structural information about the investigated molecules as conventional IR spectroscopy, but without the influence of, e.g., solvent effects and there is no "blind spectroscopic window" where no analyte bands can be observed because of solvent absorption. [107–109] Nonetheless it has its own characteristic problems. Since it is a type of action spectroscopy, the consequence of light absorption is measured, here fragmentation. The fragmentation efficiency has not to be proportional to the absorption efficiency, therefore intensities of resulting bands need to be used with caution. This is because in gas phase, it is not possible to just measure the difference in light intensity (transmission or extinction) because the ion density in an ion trap is far too low. Instead the ions get irradiated with monochromatic light from an intense light source, in this work the free electron laser. For this the Paul trap of the amaZon ETD mass spectrometer at FELIX, used for this kind of experiments, is equipped with a trap that offers optical access: Two holes, one at the top and one at the bottom of the ring electrode provide the optical access to the ion cloud inside the trap. Two mirrors underneath the trap redirect the light after traveling through the trap out of the mass spectrometer (compare Figure 12). The timing of the measuring cycles of the mass spectrometer is matched with the timing of the laser pulses, so it is possible to control the number of pulses admitted to the ion cloud before the mass spectrum is recorded. [43, 110] If the wavenumber of the photon is resonant with a vibrational transition of the investigated ion, it absorbs the energy. Is this energy enough to get over the dissociation limit, ionic fragments can be observed. If the energy is not enough for fragmentation, the energy gets redistributed in the molecule via intramolecular vibrational redistribution (IVR) and energy of more photons can be absorbed until the dissociation limit is reached. [108] By increasing the number of laser pulses during one measurement cycle it is not possible to increase the amount of photons for one dissociation event, because the IVR life time is much shorter than the time between to pulses. But it is possible to increase the number of dissociation events, i. e. the number of fragments that get detected at the end of one cycle. The intensities of the precursor ions (I_{abs}^{pre}) and the fragment ions ($I_{abs}^{fra_i}$) are then evaluated with each other to get the total fragment yield (TFY) at any given wavenumber (eq. (20)).

$$TFY(\tilde{\mathbf{v}}) = \frac{\sum_{i} I_{abs}^{fra_{i}}(\tilde{\mathbf{v}})}{I_{abs}^{pre}(\tilde{\mathbf{v}}) + \sum_{i} I_{abs}^{fra_{i}}(\tilde{\mathbf{v}})}$$
(20)

Since fragments are detected from the MS, it is also called action spectroscopy. Plotting the TFY against the corresponding wavenumber provides a gas phase IRMPD spectrum.

2.1.6 Ultraviolet photodissociation

Ultraviolet photodissociation (UVPD) is a method to measure spectra of isolated molecules in the gas phase in the UV/Vis wavelength regime. Since photons in this range possess enough energy to achieve electronic transitions, it can provide information about the electronic, but also geometrical structure of molecules. It offers similar advantages in comparison to condensed phase UV/Vis spectroscopy as the IRMPD method (e.g., no solvent effects), but also similar challenges to overcome (e.g., too low absorption, compare chapter 2.1.5). Since these two methods are related only a brief introduction into the method and the differences between IRMPD and UVPD will be given. In this work, the measurements were carried out at an amaZon Speed, which was modified with two holes and two mirrors underneath for optical access (see Figure 12). As a powerful light source an UV/Vis OPO laser system (EKSPLA NT 242¹) was used. For the measurements the laser system was used in a static way, meaning that one wavelength was set and afterwards mass spectra were recorded for 1 min, before going to the next wavelength. The right timing of the laser pulses irradiating the trap was achieved by using a shutter, which is synchronized to the measurement cycle of the MS, to let the light through, when the ions are already isolated. The setup was already described in more detail in literature. [43, 111, 112]

Light in the UV/Vis range has higher photon energy than in the IR range. Therefore,

¹https://www.topag.de/products/lasers/tunable-nanosecond-lasers/nt240



Figure 12: Paul trap with the modification that enables optical access. The red line shows the optical pathway through the trap and again outside of the spectrometer. [43]

one could encounter fragmentation without energy redistribution. This is a difference to methods that require step-wise energy uptake till a dissociation barrier is reached like IRMPD or CID. Thus, it can happen to observe different fragmentation pathways, which can provide complementary information about the structure of the molecule or, more specific, the chromophors absorbing the energy. The evaluation is done by using a similar formula as for IRMPD, but the photon flux has to be taken into consideration. Therefore a correction in dependency of the wavelength is added. Additionally a fragment specific evaluation was done, meaning the relative intensity of the occurring fragments were calculated as well after equation (21). By considering fragment specific spectra, it is possible to obtain additional information about fragmentation pathways and absorption properties of the molecules. Since in the measured region (220 - 400 nm) the laser system switches between two beam generation modes at 300 nm, it is needed to scale the two parts with respect to each other to match both before joining them to a single continuous spectrum.

$$Y_{rel}^{fra_i}(\lambda) = \frac{I_{abs}^{fra_i}(\lambda)}{I_{abs}^{pre}(\lambda) + \sum_i I_{abs}^{fra_i}(\lambda)} \cdot \frac{\lambda}{hcE_{pulse}}$$
(21)

With the wavelength λ , the Planck constant $h = 6.62607015 \cdot 10^{-34} \text{ J} \cdot \text{Hz}^{-1}$, the speed of light $c = 299,792,458 \text{ m} \cdot \text{s}^{-1}$ and the energy of one laser pulse E_{pulse} .

2.2 Crossed beam ion-molecule velocity map imaging

The velocity map imaging (VMI) experiments described in the publication in chapter 4 was used to measure ion-molecule reactions. This specific experiment was originally built at the University of Innsbruck, [85, 113–115] but was moved to Kaiserslautern in spring 2021. Since then, several reactions have been studied. It was already described in detail elsewhere, but a short overview will be given here as well. [86] In general it consists of three parts: the ion source chamber housing the laser vaporization source, the molecular beam chamber and the VMI chamber (Figure 13). All three will be described in the following chapters.



Figure 13: Model of the crossed beam 3D velocity map imaging experiment in Kaiserslautern. On the right there is the laser vaporization source, in the middle is the VMI chamber and on the left the molecular beam chamber. [116]

2.2.1 Ion source chamber

The laser vaporization (LVAP) source in the ion source chamber is the place where the metal ions are generated. A thin foil of the metal of interest is placed on a rotating

stainless steel mount. The second harmonic (532 nm) of a Nd:YAG laser (Innolas Spitlight 200 compact) is focused onto the metal foil. The energy of the laser can be up to 5 mJ per pulse and is operated at 20 Hz. It can be attenuated by passing through a tunable $\lambda/2$ plate and a beam splitter cube. When the beam hits the target, a plasma is formed. Through a piezo valve helium gas with a pressure of ca. 7 bar is pulsed in (20 Hz) orthogonal to the laser beam, cooling the plasma. A charge separation is achieved by different electrical fields. The ions of wanted polarity afterwards pass the expansion channel. By the combination of relatively low helium pressure, short expansion channel and tuning of the electric fields, it is achieved, that only monomers and no clusters are formed. Several ion optics are used to transfer and focus the resulting ion beam into the VMI chamber and also adjust the velocity of the ions.



Figure 14: Model of the LVAP chamber, with the helium line on the right side (red arrow), the window where the laser gets through is on the bottom left (green arrow), and the way towards the VMI chamber is on the top left (blue arrow). The target is omitted in this model, but in the real experimental setup it is placed at the end of the green arrow.(adapted from [116])

2.2.2 Neutral beam chamber

For the generation of the molecular beam a piezoelectric valve is used. In a gas reservoir before the valve a background pressure of 0.5 to 2 bar can be set. In addition, the valve and with it the gas is heated to prevent condensation of gases like iodomethane

used in other projects. [117, 118] The whole setup of the valve can be moved in all directions to get the best alignment of the beam. In x- and y-direction it just needs to be set once for optimal alignment. When the valve is activated, it comes to a supersonic expansion with many collisions and consecutive adiabatic cooling within the nozzle. A skimmer is placed in front of of the valve, close enough to reach into the so called *zone of silence*. In that way only the least divergent fraction of the molecular beam with a very narrow velocity distribution is used. The distance between the valve and the skimmer can be adjusted in z-direction, depending on the type of the gas. The resulting molecular beam is directly transferred into the VMI chamber.



Figure 15: Model of the molecular beam chamber. On the right there is the gas inlet with the orange screws to adjust it in the xy-plane. Top left is the Piezo valve followed by the skimmer (compare labeling).(adapted from [116])

2.2.3 Velocity map imaging

In the velocity map imaging (VMI) chamber the two beams are overlapped, spatially and temporally. This happens inside a stack of six VMI electrodes. From bottom to top these are: A repeller plate to accelerate the ions to the top. Four ring shaped focusing lenses,

whereby the first one has reaction holes inside, to let the molecular beam, the ion beam and potential other beams (e.g., an electron beam) into the reaction zone. At the top is a ground plate, to ensure no electric fields penetrate into the flight tube. At the end of the flight tube there is a *microchannel plate* detector (MCP) followed by a



Figure 16: Model of the VMI chamber, showing the six VMI electrodes at the bottom and the detector system at the top. The camera is omitted at this drawing. The blue arrow and the yellow arrow show where the ion beam and the molecular beam respectively come from. The purple arrow is the direction of the acceleration towards the detector system after the reaction. (adapted from [116])

phosphor screen and a photomultiplier tube (PMT). The flight tube has a window at the top and a camera is placed above, outside of the vacuum.

For an experiment, first the neutral beam is characterized, by ionizing the neutral molecules with the electron gun and measuring their velocity. Typical values received are in Table 2. The next step is characterizing and optimizing the ion beam. Therefore, the voltages applied to the different ion optics along the pathway of the ion beam are tuned, until the target velocity with a reasonably low spread is obtained. Another value that is tuned, is the angle and its distribution of the ion beam in relation to the camera. This is important for spatial overlap with the neutral beam. Typical values are Table 3.

Both beam characterizations are done with the respective other beam turned off. The next step is overlapping both beams temporally to ensure that ions and molecules collide and subsequently react. Afterwards, all products have a given velocity, depending on the energy of the whole system and its redistribution, and expand in the Newton sphere. The whole sphere gets accelerated from the VMI electrodes towards the deTable 2: Typical values from the neutral beam characterization of CO₂.

CO ₂ beam characterization			
<i>v</i> in m/s	711 ± 52		
<i>E</i> in meV	119 ± 17		
angle in °	$\textbf{18.5} \pm \textbf{2.3}$		

Table 3: Typical values from the ion beam characterization of Nb^+ at the relative collision energy of 2.2 eV.

Nb ⁺ beam characterization			
v in m/s	$\textbf{2234} \pm \textbf{64}$		
<i>E</i> in meV	2403 ± 144		
angle in °	163.6 ± 0.9		

tector assembly. The electric fields focus ions with the same velocity vectors onto the same spot of the detector, independently from the starting point. The MCP converts an arriving ion into an electrical signal and the camera detects the position of the resulting light emission of the phosphor screen in *x*- and *y*-direction (v_x and v_y). To calibrate the detector for its zero point, residual gas in the VMI chamber is ionized by electron impact at room temperature. The PMT detects the time of arrival, from which v_z can be obtained. Only single hits can be analyzed afterwards, meaning when two or more ions are detected at the same time, these cannot be assigned individually and are therefore not used. Typically 1000 cycles are recorded which is called foreground, and afterwards the molecular beam is temporally shifted, that it does not have overlap with the ion beam anymore. Then 1000 background measurements are recorded which are subtracted from the foreground. This measurements take about 50 s each and are recorded and summed up for several minutes, up to 1 h. Then the acquisition is stopped and the ion beam is characterized again to ensure no shifts in energy or angle occured.

2D velocity distributions and angle of the two reactant beams are measured individually and fitted afterwards. A center of mass transformation is performed to transfer the velocity vectors v from the laboratory system, giving relative velocity vectors u. For the product distribution, cylindrical symmetry is assumed and together with the time of flight velocity vector v_z , the full three dimensional Newton sphere is recovered mathematically. It should be noted, that this distribution is weighted by v_r^{-1} . Comparable sliced images then are plotted as 2D histograms using v_x and v_r . Here, nonphysical velocities aren't taken into consideration, i.e., ions which have more translational energy than the sum of reactant kinetic and internal energy and exothermicity of the reaction. Integration of the original distributions over scattering angle or energy give 1D histograms of energy and scattering angle, respectively.

This method offers several advantages compared to other techniques. The first is the possibility to measure differential state to state reaction cross sections. The infor-

mation about the product state can be directly derived from its velocity, which is not the case for other experiments like guided ion beam. [119] Furthermore, the measurement of the full Newton sphere, instead of using a rotatable detector measuring one laboratory angle after another, not only accelerates data acquisition, but also decouples the event rate from the angular resolution. [120, 121] Together with the high angular and energy resolution, VMI is a great technique for studying the dynamics of bimolecular ion molecule reactions.

3 Mass spectrometry based investigations on complexes of the type M(dgpy)₂

3.1 Gas-Phase Characterization of Redox-Active Manganese Complexes

Preamble

The following chapter consists of the publication "Gas-Phase Characterization of Redox-Active Manganese Complexes". It is all about various mass spectrometric measurements to investigate different intrinsic properties of ionic species from the 3d transition metal complex [Mn(dgpy)₂](PF₆)₄. The measurements consisted of ETD, CID, UVPD and ion-molecule reactions. The mangenese(IV) complex was the first studied of a row of six complexes with the same ligand system.

The publication is in cooperation with the group of Katja Heinze (JGU Mainz), where Nathan East did the synthesis and afterwards provided some of the solid as well as the solution phase UV/Vis data, shown in the paper.

The second cooperation was with Philipp Weber and Christoph Riehn (RPTU Kaiserslautern-Landau, Kaiserslautern) who measured and evaluated the UVPD data shown in the publication.

My part consisted of measuring and evaluating the mass spectra, ETD spectra, CID curves, and ion-molecule reactions, as well as writing the initial manuscript. During the time of those measurements the bachelor thesis of Lisa Berg and the student research internship of Adela Ceman took place, where both did some of the experiments under my supervision. Jennifer Meyer contributed to the analysis of the experimental data and the initial manuscript, and was in charge of the revisions.

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Gas-Phase Characterization of Redox-Active Manganese Complexes

Maximilian E. Huber, Adela Ceman, Philipp Weber, Lisa Berg, Nathan R. East, Christoph Riehn, Katja Heinze, and Jennifer Meyer*



ABSTRACT: Manganese complexes exhibit a rich redox chemistry, usually accompanied by structural reorganization during the redox processes often followed by ligand dissociation or association. The push-pull ligand 2,6-diguanidylpyridine (dgpy) stabilizes manganese in the oxidation states +II, +III, and + IV in the complexes $[Mn(dgpy)_2]^{n+1}$ (n = 2-4) without change in the coordination sphere in the condensed phase [Heinze et al., Inorganic Chemistry, 2022, 61, 14616]. In the condensed phase, the manganese(IV) complex is a very strong oxidant. In the present work, we investigate the stability and redox activity of the Mn^{IV} complex and its counterion (PF₆) adducts in the gas phase, using two modified 3D Paul ion trap mass spectrometers. Six different cationic species of the type $[Mn^{x}(dgpy)_{2}(PF_{\delta})_{y}]^{n+}$ (x = II, III, IV, y = 0-3, n = 1-3) could be observed for the three oxidation states Mn^{IV} , Mn^{III} , and Mn^{II} , of which one observed complex also contains a reduced



dgpy ligand. Mn^{II} species showed the highest relative stability in collision induced dissociation and UV/vis photo dissociation experiments. The lowest stability is observed in the presence of one or more counterions, which correlates to a lower total charge n+. Gas phase UV/vis spectra show similar features as the condensed phase spectra only differing in relative band intensities. The strongly oxidizing Mn^{IV} complex reacts with triethylamine (NEt₃) in the gas phase to give Mn^{III} , while Mn^{III} species show little reactivity toward NEt₃.

KEYWORDS: gas-phase, electrospray ionization, collisions, mass spectrometry, UV/vis, reactivity

INTRODUCTION

Chemical transformations at the industrial scale commonly rely on catalysis to be economical. Economical is measured in terms of input costs which refer to energy consumption and molecular efficiency. Today there is a renewed emphasis on atom efficiency, by suppressing any competing reactions. In other words, we aim the in situ formation of an activated species with a predefined reactivity, i.e., by photoactivation or by a charge transfer like in electrochemical applications. Additionally, we aim for the use of abundant and ideally nontoxic elements. Therefore, a lot of interest has been placed in employing elements of the 3d series in catalytic applications.¹⁻⁴ If transition metal complexes are used as catalysts, this requires them to be stable in their inactive and active configurations, which might refer to two different oxidation/charge or electronic states. In the present study, we investigate a redox active manganese complex. Manganese is the 12th most abundant element in the Earth's crust.⁵ It is an essential element for human biochemistry^{5,6} but also shows a wide area of application, for example, in steel production, catalysis,⁸ and batteries.⁹ The latter two take advantage of the rich redox chemistry that manganese ions possess (oxidation states of -III to +VII).^{10,11} Most complexes with higher oxidation states contain oxido ligands.¹² Only few complexes containing Mn^{II}, Mn^{III}, or Mn^{IV} ions with a [MnN₆]

coordination are known and characterized.13-15 The transitions from one oxidation state to another are most commonly accompanied by structural reorganization of the coordination sphere. Thus, only one type of complex series [Mn^{II,III,IV}(N)₆] is known, to the best of our knowledge, that preserves a pseudo-octahedral coordination geometry throughout the redox steps from Mn^{II} to Mn^{III} and Mn^{IV}, which is the complex $[Mn(dgpy)_2](PF_6)_4$ synthesized in the Heinze group^{16,17} (see Figure 1 for a schematic of the complex). This was achieved by use of the push-pull ligand 2,6diguanidylpyridine (dgpy) which is able to stabilize both low and high oxidation states. $^{18-22}$ Heinze and co-workers structurally characterized the complex in its three oxidation states. The ligand allows for relaxation of the Mn-N bond lengths and thereby accommodates structural changes related to the nature of the individual oxidation states. Hence, the complex can undergo several redox cycles without degradation

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and thereby meeting one of the criteria mentioned above. They further investigated the redox properties and photochemical reactivity of the complex.^{16,17} The complex in its Mn^{IV} configuration is of deep purple color, and it shows panchromatic absorption. Especially the Mn^{IV} complex shows a high Mn^{IV}/Mn^{III} redox potential already in its ground state ($E_{1/2} = 0.56$ V vs ferrocene),¹⁶ but following photo excitation, the oxidative potential increases further (estimated as E^*_{red} ^{(*4}Mn^{IV}/Mn^{III}) ≈ 2.0 V vs ferrocene).¹⁷

Condensed phase is a complex environment, and the interaction with the solvent as a whole and individual solvent molecules has varying impacts on the observed properties and reactivity. The transfer into gas phase, the ultimately noninteracting environment, allows us to trace intrinsic properties of the complex. The gas phase is an inert environment. Thus, gas phase experiments provide the opportunity to investigate complexes and/or reactions without influence of solvent effects. The structure-reactivity correlations derived from gas phase experiments might not be directly transferable to the solution phase but they help to build the foundation to understand complex chemical transformations in a bottom-up approach by disentangling individual effects.²³⁻ The knowledge on the molecular composition of the reactants from their m/z ratio and isotope pattern is an advantage over solution studies and can be, for example, used for isotopic labeling or HD exchange experiments.^{27,28} Electrospray ionization (ESI) mass spectrometry has been shown to be a versatile technique to investigate reaction mechanisms mediated by transition metal complexes.^{29–35} A chemical transformation generally consists of several elementary reactions, which means it involves a number of reactive intermediates. These intermediates are often low in abundance, short-lived, and thus challenging to characterize directly in a reaction mixture. ESI-MS has proven to be an efficient tool to track such intermediates by sampling the reaction mixture.^{24,36,37} The "in situ" preparation of reactive intermediates falls into two categories depending on the activation step. Photochemical activation is either achieved by illumination immediately prior to transferring the ions into the vacuum, i.e., within a capillary in front of the needle or the spray region, or by illumination within the ion trap tracking the dissociation pathways.^{23,38–45} The alternative is to react the precursor of choice within the ion trap with a neutral reactant and monitor the charged reaction products.^{30,46}

Here, we present the gas phase characterization of multiply charged ions and charged ion pairs derived from the $[Mn(dgpy)_2](PF_6)_4$ complex. We characterize the complexes in three stable oxidation states Mn^{IV} , Mn^{III} , and Mn^{II} using a Paul trap mass spectrometer. Collision-induced dissociation

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(CID) studies gauge the relative stability of the individual oxidation states with respect to each other. The primary fragmentation channel is the loss of an intact neutral dgpy ligand. UV/vis photo dissociation (UVPD) spectra have been recorded and are compared to their condensed phase counterparts. Fragmentation patterns from CID and UVPD are nearly identical, indicative of thermal fragmentation pathways in both cases. Finally, the reactivity of Mn^{IV} and Mn^{III} species with triethylamine (NEt₃) is studied in a Paul trap mass spectrometer to give first insights into the redox reactivity in the gas phase.

RESULTS AND DISCUSSION

ESI mass spectra of the complex $[Mn(dgpy)_2](PF_6)_4$ showed several species with different oxidation states of the manganese ion (x) and with different numbers of PF_6^- counterions attached (y). The resulting total charge (n+) of the observed ions differs, and therefore, in this work the examined species will be abbreviated as [x,y]n+ (see Table 1). The obtained

Table 1. Assignments of All Observed Ionic Complex Species Obtained by ESI-MS of an Acetonitrile Solution of $[Mn(dgpy)_2](PF_6)_4$ in Concentrations of 10^{-5} to 10^{-3} mol $L^{-1\alpha}$

m/z	Assignment	Abbreviation
253.8	$[Mn(dgpy)_2]^{3+}$	[III,0]3 +
380.7	$[Mn(dgpy)_2]^{2+}$	[II,0]2+
525.6	$[Mn(dgpy)_2](PF_6)_2^{2+}$	[IV,2]2+
761.4	$[Mn(dgpy)_2]^+$	[II,0]1+
1051.3	$[Mn(dgpy)_2](PF_6)_2^+$	[III,2]1+
1196.3	$[Mn(dgpy)_2](PF_6)_3^+$	[IV,3]1+

^aSee Figure S2.

mass spectra are strongly dependent on the sample concentration. While at commonly used concentrations in the 10^{-5} mol L⁻¹ range only m/z signals belonging to Mn^{III} species were observed, increasing the concentration to 10^{-3} mol L⁻¹ also allowed us to find m/z signals associated with Mn^{IV} species (see Figures 2 and S1). Figure 2 shows a typical mass spectrum, as well as the associated electron transfer



Figure 2. Overview mass spectrum of the solution of the complex $[Mn(dgpy)_2](PF_6)_4$ with an insert of the spectrum after an ETD process with [III,0]3+. Signals marked with * do not contribute to this work but have been assigned as well (see Figure S1, Table S2).

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dissociation (ETD) spectrum of [III,0]3+. It is important to mention that we could observe the two species [II,0]1+ and [II,0]2+ only after reduction via ETD. We assign [II,0]1+ as a Mn^{II} complex too, but with a reduced dgpy ligand (see Figure S3a and discussion below). Furthermore, it was neither possible to observe any species with exactly one PF_6^- unit (y = 1) nor a Mn^{IV} species without counterions. A number of other species (marked with *) were identified as well but do not contribute to this work (see Table S1).

Relative Gas Phase Stability. For all six species shown in Table 1 the collision-induced dissociation (CID) breakdown curves were measured from 0 to 3 V excitation amplitude, and the resulting fragment spectra were analyzed. Figure 3 shows



Figure 3. CID breakdown curves of the six measured species; only decrease of parent ions is depicted (appearance curves of the fragments are shown in Figure S5). The relative intensities are plotted against the mass and charge corrected E_{COMz} values (see eqs 5 and 6).

the decreasing relative ion signals of the corresponding parent ions. It was taken into consideration that ions of different mass and charge experience different acceleration in the electrical field. Therefore, the excitation energy was transformed in E_{COMz} values (see eq 6 and methods for details). The $E_{COMz}^{50\%}$ values, which describe the point where 50% of the precursor ion is fragmented, can be used as a measure for relative stability in the gas phase. Values resulting from this transformation are not quantitative but qualitative. They show a trend in relative stability but give no absolute numbers, e.g., for bond (dissociation) energies. The two species [II,0]2+ and [III,0]3+ without counterions are more stable than the ones with counterions or the reduced ligand species [II,0]1+. Among a specific oxidation state of the manganese ion, the species with less counterions is more stable. This is most likely caused by a lower dissociation barrier when a higher number of counterions is present in the complex ion pair, which successively reduces the overall charge and lowers the minimum voltage needed to cause fragmentation. A second conceivable scenario is a chemical reaction between the complex and the respective counterion assisted by the additional energy provided by the collisions during the CID time window. This leads to a kind of associative or intermediate associative substitution leading to the dissociation of the dgpy ligand followed by counteranion association, similar to a nucleophilic substitution reaction at a carbon atom. Fragmentation patterns for the most species are similar,

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consisting of loss of a neutral or positively charged ligand, loss of PF₅ (dissociation of a PF₆⁻ counterion into a F⁻ counterion and PF₅) or a combination of those (compare Figure S3b,c).

We would also like to highlight that even though [II,0]2+ has the highest relative gas phase stability fragmentation almost completely occurs in a small window of excitation energy and without appreciable detection of any ionic fragments. We consider two scenarios likely which can lead to such low mass fragments: (1) significant fragmentation of the ligands' carbon backbone or (2) the main fragmentation channel might be associated with loss of both intact neutral dgpy ligands and an Mn^{2+} ion, which m/z value of 27.5 is below the minimum detectable m/z value in the present experiment. Experimental details are given in the Supporting Information. As already mentioned at the beginning of this section [II,0]1+ was generated through a two electron reduction of [III,0]3+. During fragmentation, we observed three completely new ionic fragments: (1) loss of one guanidyl moiety $(C_7H_{12}N_3)$ giving m/z 623.2, (2) loss of one 2-guanidylpyridin moiety $(C_{12}H_{15}N_4)$ giving m/z 546.2 (which are a result of fragmentation of the ligand itself), and (3) loss of one whole neutral ligand giving m/z 408.2 (Figure S3a). It is the only case where we observed fragmentation of the ligand itself while still being coordinated to the manganese ion. Further, we did not observe a cationic ligand species dissociated from the complex as a fragment ion. Therefore, we assume the ligand to be somehow destabilized, which is why we propose that this signal could be assigned to a Mn^{II} species with one reduced ligand. Reduction of ligands containing pyridine moieties in fact was already described in the literature.53 Since we cannot prove our assumption in this case, further investigations in combination with quantum chemical calculations are needed.

Gas Phase UV/vis Spectroscopy. UVPD (Ultraviolet photodissociation) spectra were recorded for all six investigated ionic species in the range from 220-645 nm. Since the fragmentation yield is necessary to calculate gas phase UV/vis spectra, we also compared the laser-induced fragmentation patterns with the CID results in Figure 4. For each oxidation state, the fragmentation spectra of one species is shown as example. [II,0]2+ did not show any photo dissociation, therefore no spectrum could be recorded with this approach. This is in line with this species being the most stable in CID



Figure 4. Comparison of fragmentation behavior of [II,0]1+ (left: a,d), [III,0]3+ (middle: b,e), and [IV,2]2+ (right: c,f) from CID (top: a-c) and UVPD (bottom: d-f). For all species, the same fragments with similar intensities are observed.

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experiments as well. The fragmentation pathways of the remaining manganese complexes for UVPD match the CID results and therefore can be referred to as thermal fragmentation. The resulting spectra of the total fragment yields in dependency of the wavelength together with error bars are depicted in Figure 5. The power-dependent



Figure 5. UVPD spectra of (a) [II,0]1+, (b) [III,0]3+ and [III,2]1+, and (c) [IV,2]3+ and [IV,3]1+ from 220 to 650 nm. Condensed phase spectra taken in solution (CH₃CN) in the same absorption range are shown in comparison (colored area). Condensed phase spectra are taken form ref 16.

measurements at 320 and 450 nm for the species [II,0]1+and [III,0]3+ indicate no significant laser-induced fragmentation (compare Figure S9). Therefore above 405 nm, only the spectra of [III,2]1+, [IV,2]2+, and [IV,3]1+ will be considered. All spectra show maxima at about 225, 260, and 305 nm, some of them only visible as shoulderlike features, especially in the case of the Mn^{IV} species. Time-dependent density functional calculations (TD-DFT) suggested already that these are mostly ligand-centered transitions.¹⁶ [II,0]1+

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shows absorption up to 400 nm which was also observed for the condensed phase spectrum of the colorless solution of $[Mn(dgpy)_2](OTf)_2$. For the two Mn^{III} species only one ([III,2]1+) shows absorption up to 450 nm. In solution, a weak, broad band at 450 nm was assigned to a combination of different ligand-to-metal charge transfer transitions. [IV,2]2+ and [IV,3]1+ exhibit in gas phase an additional broad maximum at about 500 nm that was also observed in the condensed phase. Note that in general the UVPD spectra exhibit a strong decrease in the wavelength region above 350 nm, which we (partially) assign to the steadily decreasing photon energy preventing strong fragmentation from this region onward. These findings are in good agreement with the condensed phase spectra, referring to the position of the absorption maxima and absorption ranges of the different oxidation states.1

Gas Phase Electron Transfer Reactivity. Due to the high oxidative potential measured in condensed phase, we conducted gas phase redox reactivity measurements with [III,0]3+, [III,2]1+, [IV,2]2+, and [IV,3]1+. Our choice of reaction partner is motivated such that its vapor pressure is high enough for it to be seeded into helium in sufficient amounts but also has an ionization energy (IE) that is low enough to be oxidized by the complex ions. Triethylamine (NEt₃) has proven a suitable candidate for reaction 1 due to an ionization potential (IE) of 7.53 eV⁵⁴ and a vapor pressure of 70 hPa at 20 °C.

 $[x, y]n + NEt_3 \rightarrow [x - 1, y](n - 1) + NEt_3^{\bullet +}$ (1)

The reactions were measured at three different flow rates of reactive gas and four pulse widths t_{pulse} of the general valve, which was used to admit the NEt₃ helium mixture into the trap, for reaction times $t_{\rm trap}$ between 0 and 2000 ms (see methods for details). With the above-mentioned reaction (eq 1) in mind, one would expect two product signals, namely NEt_3^{++} (m/z 101.1) and additionally a reduced complex species if the precursor was multiply charged. We could only occasionally observe a small signal for $NEt_3^{\bullet+}$ at short reaction times that either became a secondary signal for NEt₃H⁺ (m/z102.1) or vanished completely, most likely due to reactions with impurities inside the mass spectrometer such as water or another amine radical⁵⁵ (compare Figure S6). All kinetic results are treated qualitatively because the NEt₃ density within the trap volume is currently not known. Figure 6 shows the relative intensities of the precursor complex and the observed product species for the reactions of [III,0]3+, [IV,2]2+, and [IV,3]1+ at two different pulse widths which correspond to different reactant densities for the top and bottom panels, respectively. For [III,2]1+, we observed no reaction products at all. For [III,0]3+ we see almost no reaction at short pulse width (Figure 6a) and a small increase to about 10% relative intensity of the product at the highest reaction time and longest pulse width (Figure 6d). These results imply a fairly small oxidative potential, as expected for the already reduced Mn^{III} species. $[\hat{IV},\!2]2\!+$ shows an offset of the relative intensity of 25% (Figure 6b) and 65% (Figure 6e) that has already reacted at the start of the measured reaction time. This is due to the fact that ion accumulation and isolation processes of the mass spectrometer need a finite amount of time (usually < 40 ms) in which the reaction already takes place. We see an increase of product intensity after the longest reaction time from 30% to 95%. A seemingly similar reactivity is observed for [IV,3]1+, with an offset at 0 ms reaction time and an increase



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Figure 6. Reactions of [III,0]3+ (a,d), [IV,2]2+ (b,e), and [IV,3]1+ (c,f) with NEt₃ for $t_{pulse} = 200 \ \mu s$ (a-c) and 230 μs (d-f) from 0 to 2000 ms. Example mass spectra of the appearing and evaluated product ions are given in Figure S7.

in product intensity from short to long gas pulse width. In contrast to [IV,2]2+, the product intensity at short pulse width (Figure 6c) stays almost constant during the reaction. However, it should be mentioned that [IV,3]1+ shows two unexpected products, namely [Mn(dgpy)₂(PF₆)₃(NEt₃)]⁺ at m/z 1297.4 and $[Mn(dgpy)_2(PF_6)_2(NEt_3)(-H)]^+$ at m/z1151.4 (see Figure S8). The former either could be just an adduct of a neutral NEt_3 moiety or a Mn^{III} species with a NEt3⁺⁺ adduct. In the case of the second observed product, it also is unclear whether the redox reaction took place, but in addition, a formal loss of PF6 and H+ is observed. We attempted to isolate both products to get more information through their respective fragmentation patterns, but both vanished completely on the time scale of the isolation process. Therefore, both product intensities were combined for the evaluation of the relative intensities of precursor and product. If both products are analyzed separately, we observe a higher intensity for the heavier product at short pulse width and an inverse behavior at long pulse width (see Figure S8). Therefore, one could imagine a multistep process like a proton-coupled electron transfer (PCET)^{56,57} consisting of consisting of addition of a NEt3⁺⁺ moiety to the precursor ion including the redox process giving the intermediate species $[Mn-(dgpy)_2(PF_6)_3(NEt_3)]^+$. The second step would be the dissociation of PF_6^- and H^+ originating from the amine radical cation⁵⁵ resulting in the product $[Mn(dgpy)_2(PF_6)_2(NEt_3)-(-H)]^+$ (eqs 2 and 3). Either way, due to the fact that it was neither possible to isolate the two products nor to observe any other, we were unable to identify if a redox reaction is taking place. The offsets in product intensity seen for [IV,2]2+ and [IV,3]1+ already show their high reactivity as expected from condensed phase experiments.^{16,17}

$$[\mathrm{Mn}^{\mathrm{iv}}(\mathrm{dgpy})_2(\mathrm{PF}_{6})_3]^{\mathsf{T}} + \mathrm{NEt}_3 \rightarrow [\mathrm{Mn}^{\mathrm{iii}}(\mathrm{dgpy})_2(\mathrm{PF}_{6})_3](\mathrm{NEt}_3^{\mathsf{T}})^{\mathsf{T}}$$

$$(2)$$

$$\rightarrow [Mn^{III}(dgpy)_2(PF_6)_2][(Et_2N-CH-CH_3)^{\bullet}]^+ + HPF_6$$

 $[Mn^{III}(dgpy)_2(PF_6)_3](NEt_3^{\bullet+})^+$

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EXPERIMENTAL SECTION

Electrospray Ionization (ESI) Mass Spectra. The complex $[Mn(dgpy)_2](PF_6)_4$ was synthesized as described previously¹⁶ and used as obtained for sample preparation. Sample solutions were prepared with typical concentrations of $10^{-3}-10^{-5}$ mol L⁻¹ using dried and degassed acetontrile. Experiments were performed at a modified ESI-MS (AmaZon ETD, Bruker Daltonics) with a self-built gas mixing unit. The sample solution was infused continuously into the spray chamber at flow rates of 100–180 μ L h⁻¹. A nebulizer pressure in the range of 250–700 mbar and a dry gas flow of 4 L min⁻¹ at 180 °C (both nitrogen) were applied. The potential bias between the ESI needle and spray shield was set to 4 kV. The mass spectrometer is equipped with an chemical ionization (CI) source for electron transfer dissociation (ETD) experiments. For ETD experiments, the target ions were trapped inside the Paul trap for up to 300 ms to allow for sufficient electron transfer. All experiments were performed at room temperature.

Collision-Induced Dissociation (CID). Collision-induced dissociation (CID) is used to induce fragmentation in a chosen precursor ion. Ions are stored in the 3D Paul trap of the mass spectrometer by a combination of DC voltage and radio frequency (RF). By increasing the RF amplitude, the trapped ions are accelerated. Repeated collisions with the helium buffer gas transfer kinetic energy form the collisions into rovibrational degrees of freedom, which following internal vibrational redistribution (IVR) subsequently leads to fragmentation of the weakest bond.^{58,59} To record so-called CID breakdown curves, the excitation amplitude (E_{LAB}) was increased stepwise from 0 to 3 V in 0.02 V steps. Mass spectra were recorded and averaged for 18 s at every amplitude. Relative intensities are calculated according to eq 4:

$$I_{\rm rel}^P(E_{\rm LAB}) = \frac{\sum_i I_{\rm abs}^P(E_{\rm LAB})}{\sum_i I_{\rm abs}^{P_i}(E_{\rm LAB}) + \sum_i I_{\rm abs}^P(E_{\rm LAB})}$$
(4)

with $I_{abs'}^p$ the absolute intensity of the parent ion, and $I_{abs}^{F_i}$ the absolute fragment intensities. The instrument specific voltage applied as excitation amplitude⁶⁰ was corrected in two steps to take into account different masses (eq 5) and different charge states *z* of the precursor complex ions (eq 6) (compare Figure S4).

$$E_{\rm COM} = E_{\rm LAB} \times \frac{M_{He}}{M_{He} + M_{\rm ion}}$$
(5)

$$E_{\rm COMz} = E_{\rm COM} \times z \tag{6}$$

The intensities were fitted with the sigmoidal function given in eq 7. The obtained $E_{\rm COMz}^{50\%}$ value is where half of the parent ions are fragmented, and it can be used as a qualitative measure for the relative stabilities of ions of chemically comparable structure.^{61–63} The parameter A describes the fitted intensity of the parent ion and the exponent the slope of the sigmoid curve.

$$I_{\rm fit}^{P}(E_{\rm COMz}) = \frac{A}{1 + e^{-B(E_{\rm COMz} - E_{\rm COMz}^{50\%})}}$$
(7)

UV Photodissociation Spectra. Photo dissociation measurements were conducted using a modified Paul trap mass spectrometer (AmaZon Speed, Bruker Daltonics)^{49,64,65} using an UV/vis OPO laser system (EKSPLA NT 242).⁶⁶ The

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2646

(3)

UV photo dissociation (UVPD) spectra were obtained by trapping the target ion for 150 ms, and laser pulses were directed through the trap overlapping with the ion cloud. The wavelength λ was varied stepwise with 2 nm per step from 220 to 405 and 10 nm steps from 405 to 650 nm. At each step, the energy of the laser pulses was set to $E_{\text{pulse}} = 1 \ \mu$ J for the lower area (\leq 405 nm) and $E_{\text{pulse}} = 5 \ \mu$ J for the higher area (>405 nm), with a statistical error of 3% at each data point. Mass spectra were recorded for 1 min and total fragment yields Y_{tot} were calculated in dependency of the wavelength λ according to eq 8.

$$Y_{\text{tot}}(\lambda) = \frac{\sum_{i} I_{\text{abs}}^{I_{i}}(\lambda)}{\sum_{i} I_{\text{abs}}^{I_{i}}(\lambda) + I_{\text{abs}}^{P}(\lambda)} \times \frac{\lambda}{hcE_{\text{pulse}}}$$
(8)

with $\frac{\lambda}{\mathrm{hcE}_{\mathrm{pulse}}}$ normalizing the spectrum with regard to photon

flux and pulse energy. The resulting total fragment yields for each point were averaged, and the corresponding standard deviations were used to denote the error. To account for differences in the beam generation method, the spectrum was scaled to overlap the measured points at 299 nm/300 nm and 404 nm/405 nm. Additionally static measurements in dependency of the pulse-energy of the laser were conducted at 245, 320, and 450 nm (see Figure S9, Table S3).

Electron Transfer Reactions. The reactions in gas phase were conducted inside the Paul trap. We modified the mass spectrometer to introduce small molecules, based on the example of Koszinowski et al.47 However, quantitative kinetic information requires careful calibration of the density of the neutral reactant within the interaction volume, that is, within the trapping volume.^{47,48} Here, we describe the key aspects of the modification, as well as the general procedures for our gas phase reactivity measurements. A reactive gas or a liquid with a sufficient vapor pressure is transferred into a gas cylinder (V =0.5 L). Afterward, the cylinder is filled with helium up to a pressure of about 5 bar. This gas mixture is directed through an auxiliary mass flow controller (Aux) that is identical to the factory set helium controller (He) built in the mass spectrometer.^{49,60} This way we can manipulate the flow of the reactive gas as a fraction of the maximum flow possible for the controller, e.g., Aux10 indicates a gas flow of 10% of the maximum flow passing through the auxiliary controller. After the flow of Aux was set, the helium flow was adjusted to result in a comparable pressure which is used for standard measurements. The pressure is measured at the chamber surrounding the Paul trap. Behind the Aux flow controller, there is a pulsed general valve (Series 9, Parker) that is controlled via an Iota One pulse driver (Parker) to tune the pulse length of the gas introduced into the trap. The signal sent was modified from $t_{\text{pulse}} = 200$ to 250 μ s in steps of 5 μ s but it should be mentioned that the general valve does not open reliably at shorter pulse lengths. In this work, only the results of the measurements with $t_{\rm pulse}$ = 200 and 230 μs are shown, as at higher pulse lengths whether no significant differences were observed and even loss in resolution and ion intensity occurred. Additionally, the pulse driver receives an input signal from the mass spectrometer which controls its timing in the measuring sequence. The gas pulses generated this way are combined with the helium flow that leads directly into the Paul trap. For the acquisition, we trap the targeted ion inside the trap for $t_{\text{trap}} = 0-2000$ ms and record mass spectra for 90 s. Afterward, the relative intensities of the precursor ion (Pi) and

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the product ions (Pr) are calculated according to eq 9 with the absolute intensities of the precursor ion $I_{abs}^{p_i}$ and all product ions $I_{abs}^{p_{r_i}}$.

$$I_{\rm rel}^{P_i}(t_{\rm trap}) = \frac{I_{\rm abs}^{P_i}(t_{\rm trap})}{\sum_{i} I_{\rm abs}^{P_{r_i}}(t_{\rm trap}) + I_{\rm abs}^{P_i}(t_{\rm trap})}$$
(9)

CONCLUSIONS

We could assign the six complex species via mass spectrometric techniques as Mn^{II} , Mn^{III} , and Mn^{IV} complexes, but no Mn^{I} was found. CID experiments show the highest relative gas phase stability for the species $[Mn(dgpy)_2]^{2+}$ followed by $[Mn(dgpy)_2]^{3+}$, while the other species with counterions or the reduced ligand needed lower energies for dissociation. Due to this fact, UVPD spectra could not be obtained for $[Mn-(dgpy)_2]^{2+}$ but for all other species, showing very similar spectra compared to condensed phase measurements. Oxidative potential was found to be much higher for Mn^{IV} species than Mn^{III} according to an ion–molecule reaction with NEt₃, as expected for the higher oxidation state of the manganese ion. In addition, our newly established setup for introduction of reactive molecules into the Paul trap was able to be applied successfully. Future experiments target the oxidative photochemistry of manganese(IV) complexes using appropriate substrates and light excitation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jasms.4c00113.

(Table S1) Bond lengths of different Mn-N bonds; (Table S2) assignments of all ionic species observed in Figure S1; (Table S3) Fit parameters of allometric fits of the power-dependent measurements; (Figure S1) overview and ETD spectra of the measured solution; (Figure S2) comparison of different concentrations of the complex solution; (Figure S3) comparison of typical CID-fragmentation spectra; (Figure S4) comparison CID curves with different ordinates; (Figure S5) all CID spectra with fragment specific appearance curves and E_c^5 ^{9%}_{OM} values; (Figure S6) comparison of NEt₃• ⁺ and NEt₃H⁺ at different reaction times; (Figure S7) mass spectra of the precursor ions and products; (Figure S8) reaction of [IV,3]1+ with both products separatly; and (Figure S9) power-dependent measurements at 320 and 450 nm (PDF)

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41

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Notes

The authors declare no competing financial interest.

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Supporting Information Gas phase characterization of redox active manganese complexes

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3 Mass spectrometry based investigations on complexes of the type M(dgpy)₂

- Table S1: Bond lengths of different Mn-N bonds.
- Figure S1: Overview and ETD spectra of the measured solution.
- Table S2: Assignments of all ionic species observed in Figure S1.
- Table S3: Fit parameters of allometric fits of the power dependent measurements.
- Figure S2: Comparison of different concentrations of the complex solution.
- Figure S3: Comparison of typical CID-fragmentation spectra.
- Figure S4: Comparison CID curves with different ordinates.
- Figure S5: All CID spectra with fragment specific appearance curves and $E_{COM}^{50\%}$ values.
- Figure S6: Comparison of NEt_3^{*+} and NEt_3H^+ at different reaction times.
- Figure S7: Mass spectra of the precursor ions and products.
- Figure S8: Reaction of [IV,3]1+ with both products seperatly.
- Figure S9: Power dependent measurements at 320 and 450 nm.

Collision induced dissociation (CID) curves

For the CID process the ions inside the trap get excited by an auxiliary RF-voltage, where the amplitude is set in V and the exact frequency fits to the m/z ratio that only the ions of interest get accelerated and not the fragments. Energy distribution during collisions with helium depends on the masses of helium and the ions, therefore a correction is needed, resulting in the E_{COM} values. The energy ions get through the electrical field depends on the voltage and the charge. Due to this higher charged ions receive more acceleration and the resulting collisions with helium are harder. Because of this we corrected the E_{COM} by simply multiplying with the number of charges z, resulting in E_{COMz} (compare figure S4). We want to note that this should be correct for direct current whereas for RF-voltage the effective voltage is different but would only add a constant factor to all values and would only compress the CID curves but not change the relative progression.

Table S1: Different average bond lengths of the manganese complexes in its different oxidation states measured from single crystals in Angstrom (taken from Heinze *et al. Inorganic Chemistry* 2022, 61, 14616).

ox.state	Mn-N _{py}	Mn-N _{gu}
Mn(II)	2.291	2.193
Mn(III)	2.167	2.009
Mn(IV)	1.991	1.960



Figure S1: Overview mass spectrum of the solution of the complex $[Mn(dgpy)_2](PF_6)_4$ with an insert (a) of the received spectrum after an ETD process with [III,0]3+. Table S2 contains assignments of all observed signals.

m/z	assignment	sum formula	abbreviation
176.6	$(dgpy)^{2+}$	$(C_{19}H_{27}N_7)^{2+}$	n/a
204.1	$[Mn(dgpy)]^{2+}$	$(MnC_{19}H_{27}N_7)^{2+}$	n/a
253.8	$\left[\mathrm{Mn}(\mathrm{dgpy})_2\right]^{3+}$	$({ m MnC}_{38}{ m H}_{54}{ m N}_{14})^{3+}$	[III,0]3+
353.2	$(\mathrm{dgpy})^{1+}$	$(C_{19}H_{27}N_7)^{2+}$	n/a
380.7	$[\mathrm{Mn}(\mathrm{dgpy})_2]^{2+}$	$({ m MnC}_{38}{ m H}_{54}{ m N}_{14})^{2+}$	[II,0]2+
390.2	$[\mathrm{Mn}(\mathrm{dgpy})_2\mathrm{F}]^{2+}$	$({\rm MnC}_{38}{\rm H}_{54}{\rm N}_{14}{\rm F})^{2+}$	n/a
427.2	$[Mn(dgpy)F]^+$	$({\rm MnC_{19}H_{27}N_7F})^+$	n/a
525.6	$[Mn(dgpy)_2](PF_6)_2^{2+}$	$({\rm MnC}_{38}{\rm H}_{54}{\rm N}_{14}{\rm P}_{2}{\rm F}_{12})^{2+}$	[IV,2]2+
761.4	$[Mn(dgpy)_2]^+$	$({ m MnC}_{38}{ m H}_{54}{ m N}_{14})^+$	[II,0]1+
1051.3	$[\mathrm{Mn}(\mathrm{dgpy})_2](\mathrm{PF}_6)_2^{+}$	$({\rm MnC}_{38}{\rm H}_{54}{\rm N}_{14}{\rm P}_{2}{\rm F}_{12})^{+}$	[III,2]1+
1196.3	$[\mathrm{Mn}(\mathrm{dgpy})_2](\mathrm{PF}_6)_3^{+}$	$({\rm MnC}_{38}{\rm H}_{54}{\rm N}_{14}{\rm P}_{3}{\rm F}_{18})^+$	[IV,3]1+

Table S2: Assignments of all observed ionic species obtained by ESI-MS spectra of the solution of $[Mn(dgpy)_2](PF_6)_4$.

Table S3: The power dependent measurements (compare Figure S9) were fitted with an allometric fit with the formula $y = a \cdot x^b$. The fit parameters for 320 and 450 nm are given here. For **[II,0]1+** and **[III,0]3+** at 450 nm no fit was done because no significant photoinduced fragmentation was observed.

	320 nm		450 nm	
species	a	b	a	b
[II,0]1+	0.193 ± 0.004	0.747 ± 0.016	n/a	n/a
[III,0] 3 +	0.040 ± 0.002	0.995 ± 0.033	n/a	n/a
[III,2]1+	0.313 ± 0.017	0.657 ± 0.038	$0.001 \pm 2E - 4$	1.091 ± 0.080
[IV,2]2+	0.085 ± 0.003	0.928 ± 0.026	$0.005 \pm 3E-4$	1.117 ± 0.038
[IV,3]1+	$0.026\pm 4E-4$	1.519 ± 0.012	$4E-4\pm8E-5$	1.837 ± 0.090



Figure S2: Overview mass spectra of solutions of $[Mn(dgpy)_2](PF_6)_4$ with different concentrations from $10^{-5} - 10^{-3} \text{ mol/l}$. Only at the highest concentration (a) the signal at m/z of 1196.3 could be observed. Also the two species [IV,2]2+ and [III,2]1+ were not observed below 10^{-4} mol/l (b). At the lowest concentration (c) asignals for fragments of the complex or signals for the ligand are the most abundend.



Figure S3: Typical fragmentation spectra observed during CID measurements of the example species [II,0]1+ (a), [III,0]3+ (b) and [IV,2]2+ (c). The arrows and formula show the formal loss leading to the fragment ion signals with their m/z ratio labeled above.



Figure S4: CID curves with different calculated energies, a) the RF-amplitude given by the software, b) mass corrected E_{COM} values, c) charge corrected E_{COMz} values. In a) Mn(II) species are the most stable, while Mn(III) and Mn(IV) show the same behavior as they both fragment at lower voltages the higher the number of counterions present. The mass corrected plot b) shows a similar relativ trend with the difference that the species **[III,0]3**+ is more stable than the other Mn(III) and Mn(IV) species. Coreccted by charge (c) the triple positivly charged **[III,0]3**+ is almost as stable as **[II,0]2**+ and the reduced ligand species **[II,0]1**+ is a little less stable than the Mn(IV) species **[IV,2]2**+. Therefore we can conclude that the species **[II,0]2**+ is the most stable, lower number of counter ions ist more stable (probably due to dissipation of charge) and the reduced ligand lowers the stability of the Mn(II) species significantly.



Figure S5: CID curves of all six complex species (a - [II,0]1+, b - [II,0]2+, c - [III,0]3+, d - [III,2]1+, e - [IV,2]2+ and f - [IV,3]1+). Each containing the breakdown curve of the precursor ion and the corresponding appearance curves, where the fragment specific ones are in transparent colors. The sigmoidal fit was done for each respective precursor ion and the $E_{COM}^{50\%}$ value used as a scale for relative gas phase stability is given in each graph.



Figure S6: Comparison of mass spectra at different reaction times for the reaction of [IV,2]2+ with NEt₃ giving signals for NEt₃⁺⁺ (m/z 101.1) and NEt₃H⁺ (m/z 102.1) which both vanish at longer reaction times.



Figure S7: The three panels show example mass spectra of the precursor ions and all observed products after reaction with NEt_3 of a) **[III,0]3+**, b) **[IV,2]2+** and c) **[IV,3]1+**. The two inserts each show a zoom of the product isotopic patterns of the respective reaction and an overlaid simulation for a product of a proton transfer reaction without occurring redox reaction. We also did not see other products than those shown here. Thus, we exclude the combination of redox reaction and proton transfer for the observed reactions.

S11


Figure S8: Reaction of [IV,3]1+ with NEt₃ at Aux10 for $t_{pulse} = 200 \,\mu s$ (top) and 230 μs (bottom) from 0 to 2000 ms. The empty triangles show the two mentioned products $[Mn(dgpy)_2(PF_6)_3(NEt_3)]^+$ (m/z = 1297.4) and $[Mn(dgpy)_2(PF_6)_2(NEt_3)(-H)]^+$ (m/z = 1151.4) and a reversed intensity distribution of those for low or high puls lengths respectively.

S12



Figure S9: Power dependent measurements of all five measurable species at $320 \,\mathrm{nm}$ (left - a,c,e) and $450 \,\mathrm{nm}$ (right - b,d,f) with allometric fits.

S13

3.2 Additional investigations on complexes of the type M(dgpy)₂

The following sections presents further in depth investigations on complexes of the type $[M(dgpy)_2](X)_y$ (M = V, Cr, Mn, Fe, Co, Ni; X = PF₆, BF₄, OTf; y = 2-4). The complexes were synthesized according to the literature by Alexandra König in the working group of Katja Heinze (Department of Chemistry, Johannes Gutenberg University, Mainz) and provided to us. [81–84] The measurements of the chromium(III) complex were done by Daniel Langhauser during his bachelor thesis under my supervision. The measurements of the other complexes (V and Fe - Ni) and the respective evaluations were done solely by myself, if not stated otherwise. In this work, the following five complexes were investigated complementary to $[Mn(dgpy)_2](PF_6)_4$ (dgpy = 2,6-diguanidylpyridine) published in chapter 3.1 (Figure 17):

The vanadium(III) complex $[V(dgpy)_2](OTf)_3$, the chromium(III) complex $[Cr(dgpy)_2](PF_6)_3$, the iron(II) complex $[Fe(dgpy)_2](PF_6)_2$, the cobalt(III) complex $[Co(dgpy)_2](BF_4)_3$, and the nickel(II) complex $[Ni(dgpy)_2](BF_4)_2$. For the iron(II) complex a solution of $[Fe(dgpy)_2](PF_6)_2$ and $[Fe(Cp)_2](PF_6)$ (= Ferrocenium ion) in acetonitrile was prepared to obtain the complex $[Fe(dgpy)_2](PF_6)_3$ in situ.



Figure 17: General structural formulae of the investigated complexes: a) $[V(dgpy)_2](OTf)_3$, b) $[Cr(dgpy)_2](PF_6)_3$, c) $[Mn(dgpy)_2](PF_6)_4$, d) $[Fe(dgpy)_2](PF_6)_{2/3}$, e) $[Co(dgpy)_2](BF_4)_3$, and f) $[Ni(dgpy)_2](BF_4)_2$.

The first object was to find out which ionic species can be observed directly from solution or can be created via an ETD process. Thus, mass spectra of all mentioned

solutions were recorded, ETD experiments with multiply charged ions were conducted to created new, reduced species and all species of interest were isolated and compared to simulated spectra to confirm the assignment. To obtain information about relative gas stability of the complexes in gas phase, CID curves were measured with all obtained species. Fitting the breakdown curves provided the $E_{COM_7}^{50\%}$ values used as a measure for the relative stability (compare section 2.1.2). Furthermore, these measurements gave insights into the fragmentation pathways of the different species. UVPD spectra were measured to find out about the absorption properties of the isolated species to compare them with the solution spectra from literature, if available. Photofragmentation patterns were also compared to the results from the CID studies. Complementary to manganese, reactions with NEt₃ were measured to find out if other complex species show some reactivity as well. At the end of the chapter (section 3.3), further experiments are described that are started but not finalized, yet. One is about calibration of the neutral gas added into the Paul trap for the ion-molecule reactions. These measurements are crucial for future quantification of the kinetic studies. IRMPD measurements at the Free Electron Laser (FELIX) were carried out for the complexes $[Mn(dgpy)_2](PF_6)_4$ and $[Co(dgpy)_2](BF_4)_3$, and the solution of $[Fe(dgpy)_2](PF_6)_2$ and $[Fe(Cp)_2](PF_6)$. Here, the object was to find out more about structure of the ionic species especially about the nature of the reduced species. First evaluations of the measured data are shown, as well as first interpretations, which need theoretical results to be more reliable in the future. The last section presents first results on excited state ion-molecule reactions, measured in the master's thesis of Adela Ceman. These results are a proof of principle to show that this kind of measurement is possible with our current setup, enabling more kinetic studies in the future with the same setup and sample solution.

3.2.1 Mass spectra and ETD experiments

ESI mass spectra of all complex species were measured at the amaZon ETD, with solutions in acetonitrile in concentrations of about $10^{-3} - 10^{-4}$ M yielding reasonably high intensitiy of all species. The solutions of the complexes of the metal centers V³⁺, Fe²⁺, Co³⁺, and Ni²⁺, as well as the solution of [Fe(dgpy)₂](PF₆)₂ with [Fe(Cp)₂](PF₆) were prepared inside a glove box with degassed and dry solvent. Anyway, only the solutions of iron showed sensitivity towards oxygen and moisture in the air when stored outside of the box for more than 1 day. This sensitivity resulted in a loss of signal for the expected iron complex species and either an increase of fragments or decrease of





Figure 18: Example ESI mass spectrum of the solution of the complex $[Co(dgpy)_2](BF_4)_3$. The insert shows a magnification with the factor 100 in intensity of the area from 920 - 960 m/z because of the low intensity of the signal at m/z 939. The labelings are the complex species $[Co(dgpy)_2]^{3+}$ $(m/z \ 255)$, $[Co(dgpy)_2](BF_4)_1^{2+}$ $(m/z \ 426)$, and $[Co(dgpy)_2](BF_4)_2^+$ $(m/z \ 939)$. Comparisons of the isolated species with the simulated species are in the supplementary information (chapter 7).

Mass spectra were measured for all solutions and the main signals were assigned. The signals that belong to the complex, thus consisting of a metal center and two dgpy ligands with or without counter ions $([M(dgpy)_2](X)_y^{n+})$ were the species of interest. In Table 4 - Table 9 all observed species of interest are listed. For this work, a similar abbreviation as introduced for Mn will be used: M[x,y]n+ where M will be the metal ion (V, Cr, Mn, Fe, Co, or Ni), x the oxidation number of the metal ion in roman numbers, y the number of counter ions attached, and n the number of charges of the ionic species. Due to the similarities of all the mass spectra only one example spectrum for $[Co(dgpy)_2](BF_4)_3$ is shown in Figure 18. The other mass spectra can be found in the appendix (7.1) together with the respective ETD spectra and comparisons of the isolated and simulated isotopic patterns.

In the overview mass spectra typically three signals for species of interest could be observed: M[III,0]3+, M[III,1]2+, and M[III,2]1+. In case of the complexes $[Fe(dgpy)_2](PF_6)_2$ and $[Ni(dgpy)_2](BF_4)_2$ only the two species M[II,0]2+ and M[II,1]1+ were observed, as

it was expected due to the given oxidation state of these two central metal ions. Even though, these spectra showed the same species and thus looked very similar, this was a big difference compared to the manganese complex. As described in chapter 3.1, manganese showed different species and intensities, in dependency of the concentration, and not all expected species could be observed, e.g., species with exact one counter ion were not observed at all. It cannot be stated clear what the reason for this difference is, possibly this is a consequence of the higher oxidation state of the manganese(IV) center. Another exception to the clear and readily assignable mass spectra is that of the solution of $[Fe(dgpy)_2](PF_6)_2$ with $[Fe(Cp)_2](PF_6)$. Here, a lot of other ion signals were observed as well and also in higher intensities than the signals of interest. Most of which could be assigned to $[Fe(Cp)_2]^+$, adducts or fragments of the two complexes. This is not unusual since this solution is a mixture of two complexes, but it should still be noted.



Figure 19: Scheme of the reduction processes during the ETD experiments. See text for further explanation.

Table 4: Investigated species from the solution of $[V(dgpy)_2](OTf)_3$ with their respective formulae and abbreviation.

m/z	assignment	abbreviation
252	[V(dgpy) ₂] ³⁺	V[III,0]3+
*379	[V(dgpy) ₂] ²⁺	V[II,0]2+
453	[V(dgpy) ₂](OTf) ²⁺	V[III,1]2+
*906	$[V(dgpy)_2](OTf)^+$	V[II,1]1+
1055	$[V(dgpy)_2](OTf)_2^+$	V[III,2]1+

Table 6: Investigated species from the solution of $[Mn(dgpy)_2](PF_6)_4$ with their respective formulae and abbreviation. Adapted from chapter 3.2

m/z	assignment	abbreviation
253	[Mn(dgpy) ₂] ³⁺	Mn[III,0]3+
*381	[Mn(dgpy) ₂] ²⁺	Mn[II,0]2+
526	$[Mn(dgpy)_2](PF_6)_2^{2+}$	Mn[IV,2]2+
*761	[Mn(dgpy) ₂] ⁺	Mn[II,0]1+
1051	$[Mn(dgpy)_2](PF_6)_2^+$	Mn[III,2]1+
1196	$[Mn(dgpy)_2](PF_6)_3^+$	Mn[IV,3]1+

Table 8: Investigated species from the solution of $[Co(dgpy)_2](BF_4)_3$ with their respective formulae and abbreviation.

m/z	assignment	abbreviation
255	[Co(dgpy) ₂] ³⁺	Co[III,0]3+
*383	[Co(dgpy) ₂] ²⁺	Co[II,0]2+
426	$[Co(dgpy)_2](BF_4)^{2+}$	Co[III,1]2+
*852	$[Co(dgpy)_2](BF_4)^+$	Co[II,1]1+
939	$[Co(dgpy)_2](BF_4)_2{}^+$	Co[III,2]1+

Table 5: Investigated species from the solution of $[Cr(dgpy)_2](PF_6)_3$ with their respective formulae and abbreviation.

m/z	assignment	abbreviation
253	[Cr(dgpy) ₂] ³⁺	Cr[III,0]3+
*379	[Cr(dgpy) ₂] ²⁺	Cr[II,0]2+
452	$[Cr(dgpy)_2](PF_6)^{2+}$	Cr[III,1]2+
*903	$[Cr(dgpy)_2](PF_6)^+$	Cr[II,1]1+
1048	$[Cr(dgpy)_2](PF_6)_2^+$	Cr[III,2]1+

Table 7: Investigated species from the solutions of $[Fe(dgpy)_2](PF_6)_2$ and $[Fe(dgpy)_2](PF_6)_3$ with their respective formulae and abbreviation.

m/z	assignment	abbreviation
254	[Fe(dgpy) ₂] ³⁺	Fe[III,0]3+
*381	[Fe(dgpy) ₂] ²⁺	Fe[II,0]2+
454	$[Fe(dgpy)_2](PF_6)^{2+}$	Fe[III,1]2+
*762	[Fe(dgpy) ₂] ⁺	Fe[l,0]1+
*907	$[Fe(dgpy)_2](PF_6)^+$	Fe[II,1]1+
1052	[Fe(dgpy) ₂](PF ₆) ₂ ⁺	Fe[III,2]1+

Table 9: Investigated species from the solution of $[Ni(dgpy)_2](BF_4)_2$ with their respective formulae and abbreviation.

m/z	assignment	abbreviation
382	[Ni(dgpy) ₂] ²⁺	Ni[II,0]2+
*764	[Ni(dgpy) ₂] ⁺	Ni[II,0]2+
851	$[Ni(dgpy)_2](BF_4)^+$	Ni[l,1]2+

With the multiply charged species of all samples (charge number z = 3, 2) ETD experiments were carried out. This was to achieve reduction of those species and create new species inside the trap, which usually may be hardly or not accessible at all in condensed phase or even gas phase without a possibility to transfer electrons. Figure 19 shows three observed reduction processes. The cases a) and b) were observed for the samples with central ion oxidation state of +III or +IV, with the exception that for manganese no species like in b) was observed. The reduction process c) occured for Fe(II) and Ni(II). a) describes a one electron reduction of the triply charged species to the respective doubly charged one as well as the creation of a singly charged product that can be achieved via a two electron reduction or two reductions in sequence. Although the latter way seems more probably since each fluoranthene anion carries one electron and a three body collision is not likely to happen, it cannot be excluded. The cases b) and c) each describe a one electron reduction step, while the species with a counter ion attached belong to b) and the ones without counter ion to c). Accordingly, three new species for each of the complexes $[V(dgpy)_2](OTf)_3$, $[Cr(dgpy)_2](PF_6)_3$, $[Fe(dgpy)_2](PF_6)_3$, and $[Co(dgpy)_2](BF_4)_3$ could be obtained. For $[Fe(dgpy)_2](PF_6)_2$ and [Ni(dgpy)₂](BF₄)₂ one new species could be observed respectively. Here, one exemplary spectrum is shown for the reduction of $[Co(dgpy)_2]^{3+}$ in Figure 20, while the respective other spectra are in the appendix, as mentioned before.

With these methods it was possible to observe 30 complex species overall, including the manganese species already published. A summary with assignments for the 30 species is given in Table 4 - Table 9. The manganese species are already known from chapter 3.2 and were adapted by adding the "Mn" in front of the abbreviation. All m/z values are rounded to whole numbers and describe the highest peak in the respective isotopic pattern. Species marked with an asterisk are obtained via reduction during an ETD process.

Since for the iron complex two different solutions were used (one of the iron(II) complex $[Fe(dgpy)_2](PF_6)_2$ and one of the in situ generated iron(III) complex $[Fe(dgpy)_2](PF_6)_3)$, observed species from both solutions are combined in Table 7. The two species **Fe[II,0]2+** and **Fe[II,1]1+** are marked with an asterisk because they could be generated via a reduction from the iron(III) solution, but were also observed in the iron(II) solution without a reduction step.

During the measurements of the chromium complex $[Cr(dgpy)_2](PF_6)_3$, additional signal sets could be observed at m/z 454, 1052 and 1056. They could be identified as species with triflate counter ions which replaced the hexafluorophosphate ions. These anions were impurities from the synthesis that weren't completely removed dur-



Figure 20: Example mass spectrum after ETD experiment with the complex species $[Co(dgpy)_2]^{3+}$ (m/z 255). The labelings are the precursor as well as the complex species $[Co(dgpy)_2]^{2+}$ (m/z 383) and $[Co(dgpy)_2]^+$ (m/z 765). The arrows show the two reduction steps towards the two species of interest. There are some other signals, which are fragments originating from the ETD process.

ing ion exchange needed for the crystallization. Since the permutations of the complex $[Cr(dgpy)_2](PF_6)_3$ with OTf^- had significantly lower intensities and could be separated by isolation they are not included in Table 5.

Although in the ETD spectrum of **V[III,0]3+** and **Cr[III,0]3+** signals at m/z of 757 and 758 respectively can be seen (Figure 37 and Figure 39), it wasn't possible to isolate these. Therefore, no experiments could be performed with these species, which would refer to **V[I,0]1+** and **Cr[I,0]1+**, respectively and they are not listed.

3.2.2 Collision induced dissociation

For all additional 24 species (without the six manganese species discussed in 3.1) CID curves were measured, evaluated and compared. In the following chapter first the fragmentation pathways of the different species will be discussed for each metal at once. At the end there is a comparison with each other and the manganese results.

The CID mass spectra were measured by isolating the full isotopic pattern and afterwards applying the excitation amplitude, which was increased in steps of 0.02 V

from 0 to 3 V. At every step, mass spectra were recorded for 0.3 min and averaged afterwards. The relative intensities of the precursor ion and all relevant fragments were evaluated after equations (12) and (13). As explained in chapter 2.1.2, a transformation of the excitation amplitude to the relative E_{COMz} value was done with equations (14) and (16). The $E_{COMz}^{50\%}$ values were then derived from the sigmoidal fit (eq. (17)) of the precursor ion and used as relative measure of gas phase stability.

Typical fragmentation pathways consisted of: (1) Loss of cationic or neutral ligand, (2) dissociation of counter ions, or (3) fragmentation of counter ions leaving a F^- at the complex species. All three pathways also can occur together, for example loss of a ligand and a counter ion. Additionally, sometimes fragmentation into small fragments that could not be assigned were observed as well.

Vanadium

The vanadium(III) complex species **V[III,0]3+** shows four fragments, but most of them couldn't be assigned, only the signal of protonated ligand at m/z 353. **V[II,0]2+** instead shows a dark fragmentation, i.e., there was almost no ion intensity observed after fragmentation at all. A reason for this could be fragmentation into ions that have a lower m/z ratio than the low mass cut-off of the mass spectrometer. The species **V[III,1]2+** with one counter ion first fragments into several different ions like dgpyH⁺, **V[II,0]2+** or [V(dgpy)(OTf)(-H)]⁺, but at higher excitation amplitudes mostly the fragmentation channel into **V[III,0]3+** is observed, which means loss of the counter ion (Figure 21, gray squares).



Figure 21: CID appearance curves for all fragments of V[III,1]2+ and the sum of all fragments (TFY). At amplitudes of > 1 V V[III,0]3+ (gray squares) arises as the most intense fragment channel.

A possible explanation would be just "stripping-off" the counter ion, is a kinetically preferred pathway and therefore takes the lead at higher collision energies. V[II,1]1+ also shows the fragmentation channel associated to the loss of one ligand moiety, but the ligand is probably dissociated as a neutral molecule, because no ions with m/z 353 are observed. Other than this there are only small fragmentation channels into fragments that could not be assigned, so probably fragmentation of the ligand or the counter ion into small fragments. V[III,2]1+ also shows loss of one neutral ligand as most intense fragmentation channel. Additionally one fragment is observed, where presumably one of the triflate ions fragments, but resulting in two signal sets with a spacing of 3 m/z. One possible explanation could be different fragmentation of the triflate, leaving behind a fluorine or an oxygen, respectively (both sets are combined within the red circles in Figure 47 e). Similarly a fragment at m/z 439 is observed which was assigned to loss of a neutral dgpy and fragmentation of both counter ions leaving behind one fluorine and one oxygen each. The two additional signal sets at three m/z lower and higher, respectively could be the variation of the leftover atoms (fluorine:oxygen = 0:2, 1:1 or 2:0). This was the only case, where this fragmentation of the

triflate counter ion was observed. It also can't be stated for sure that the oxygen stems from counter ion fragmentation and not from some impurity inside the trap (e.g., water), but the variations hint towards the proposed fragmentation pathway. The relative stability of all complex species decreases with increasing m/z, resulting in **V[III,0]3+** as most stable and **V[III,2]1+** as species with the lowest $E_{COMz}^{50\%}$ value. The respective fragment specific CID appearance curves as well as the $E_{COMz}^{50\%}$ values can be found in Figure 47.

Table 10: Fragments observed and evaluated for the CID curves of the vanadium complex species. Unassigned fragments are missing here for clarity, but can be seen in the respective figures (see chapter 7). (-H) means the mass of 1 and therefore probably a hydrogen atom is missing, but without further specification about the charge state of the hydrogen ($H^{+/0/-}$). In case of **V[III,2]1+** the possible permutations are in the assignment, the m/z shows the most intense only.

Species	Fragment	m/z	$E_{COMz}^{50\%}$
V[III,0]3+	-	252	0.0190
	LH⁺	354	
V[II,0]2+	-	379	0.0124
	$V(L_2)^{3+}$	252	
V[III,1]2+	-	453	0.0102
	$V(L_2)^{3+}$	252	
	LH⁺	354	
	$V(L)_2^{2+}$	378	
	$V(L)(OTf)(-H)^+$	552	
V[II,1]1+	-	906	0.0041
	V(L)(OTf) ⁺	553	
V[III,2]1+	-	1055	0.0025
	$V(L)(O_n/F_{n-2})^+$	439	
	$V(L)(OTf)(O/F)^+$	569	
	$V(L)(OTf)_2^+$	702	
	$V(L)(OTf)_2(F)(-H)^+$	720	

Chromium

Cr[III,0]3+ shows mostly smaller fragments, probably resulting from fragmentation of the ligand. This is the reason only one of the ionic fragments could be assigned (dgpy⁺, Figure 48a, purple routes). The reduced species **Cr[II,0]2+** shows similar to vanadium

a mostly dark fragmentation. Thus, a few signals with low intensity can be observed, at low excitation amplitudes the oxidized species **Cr[III,0]3+** as well as positively charged ligand. At higher amplitudes, only a broad signal that couldn't be assigned is observed. **Cr[III,1]2+** shows typical fragmentation behavior of dissociating a ligand or a counter ion or fragmentation of the counter ion leaving behind a F^- . The reduced counterpart **Cr[II,1]1+** shows similarly fragmentation of the counter ion leaving behind a F^- and at higher amplitudes accompanied by dissociation of one neutral ligand moiety. The chromium(III) species with two counter ions (**Cr[III,2]1+**) shows dissociation of ligand, counter ions or fragmentation of the counter ions as well. At high excitation amplitudes, a new fragmentation channel opens, where a monocationic fragment arises that can not be assigned (m/z 685). Also the relative intensity with the former most intense fragment changes (gray squares and red circles, Figure 22), probably due to a faster or more favorable fragmentation of the precursor ion into this fragment. A second step is unlikely, since the new fragment has a higher mass than the former most intense [Cr(dgpy)](F)₂⁺.



Figure 22: CID appearance curves for all fragments of **Cr[III,1]2+** and the sum of all fragments (TFY). At amplitudes of > 1.5 V a new fragment which couldn't be assigned arises as the most intense fragment channel (red circles).

The relative overall stability of the five complex species, decreases with higher mass and lower charge. Only **Cr[II,1]1+** is a little less stable than **Cr[III,2]1+** even though it has the lower m/z. The reason is probably a low dissociation barrier for the counter ions and a decreased stability caused by the excess electron in case of the reduced species. The respective fragment specific CID appearance curves as well as the $E_{COMz}^{50\%}$ values can be found in Figure 48.

Table 11: Fragments observed and evaluated for the CID curves of the chromium complex species. Unassigned fragments are missing here for clarity, but can be seen in the respective figures (see chapter 7). (-H) means the mass of 1 and therefore probably a hydrogen atom is missing, but without further specification about the charge state of the hydrogen $(H^{+/0/-})$.

Species	Fragment	m/z	$E_{COMz}^{50\%}$
Cr[III,0]3+	-	253	0.0191
	L ⁺	353	
Cr[II,0]2+	-	379	0.0133
	Cr(L) ₂ ³⁺	253	
	LH ⁺	354	
Cr[III,1]2+	-	452	0.0100
	Cr(L)(gua) ²⁺	272	
	$Cr(L)(guapy)(-H)_2^{2+}$	309	
	L ⁺	353	
	$Cr(L)_{2}^{2+}$	379	
	$Cr(L)_2F^{2+}$	389	
	Cr(L)(gua)H ⁺	554	
Cr[II,1]1+	-	903	0.0029
	Cr(L)F ⁺	424	
	Cr(L) ₂ F ⁺	777	
Cr[III,2]1+	-	1048	0.0032
	$Cr(L)(F)_2^+$	443	
	$Cr(L)_2(F)(-H)^+$	776	
	$Cr(L)_2(F)_2^+$	796	
	$Cr(L)_{2}(PF_{6})(-H)^{+}$	902	

Iron

In the case of iron, species Fe[III,2]1+ could not be isolated with a sufficient intensity, therefore no CID curve was measured. Fe[III,0]3+ shows only one fragmentation pathway. Cationic ligand (L⁺) and the complementary species with iron and one ligand moiety and a charge state of 2+ (Fe(L)²⁺) are the two daughter ions. The latter decreases again at higher excitation voltages, i.e., it probably undergoes further fragmentation. The species **Fe[II,0]2+** showed almost no ionic fragments (< 1% of precursor intensity), which is the reason for the high noise in the CID curve. The observed fragmentation, mainly was positively charged ligand and a species with iron and one ligand but only singly charged ($Fe(L)^+$), but with very small abundance, as already mentioned. The same fragmentation pathways are observed for **Fe[I,0]1+**. But it also shows a very small third product, which is assigned to fragmentation of one ligand still attached to the iron, losing a guanidylpyridine (C₁₂N₄H₁₅) moiety, leaving the other guanidyl moiety bound. Also the two species with counter ions (Fe[III,1]2+ and Fe[III,2]1+) show complementary fragmentation pathways. Dissociation of ligand but with the addition that they also fragment the counter ion leaving a F⁻ attached to the resulting species (Fe(L)F⁺) was observed. They also both show a complementary fragmentation pathway without the loss of a ligand, but fragmentation of the counter ion $(\mbox{Fe}(L)_2\mbox{F}^{2+}$ and Fe(L)₂F⁺ for **Fe[III,1]2+** and **Fe[III,2]1+**, respectively). All fragments with the respective assignments as well as the $E_{COMz}^{50\%}$ values are in Table 12. Fragment specific CID curves are in the appendix in Figure 49. It can be observed that the two species Fe[III,0]3+ and Fe[II,0]2+ are significantly more stable than the other three species. Probable reasons are the weaker interaction of counter ion to complex and a destabilization from the additional electron that species **Fe[I,0]1+** got from the ETD process.

Table 12: Fragments observed and evaluated for the CID curves of the iron complex species, combining the results of both solutions measured. Unassigned fragments are missing here for clarity, but can be seen in the respective figures (see chapter 7). As stated in the text for **Fe[III,2]1+** no CID curve was received.

Species	Fragment	m/z	$E_{COMz}^{50\%}$
Fe[III,0]3+	-	254	0.0130
	Fe(L) ²⁺	205	
	L ⁺	353	
Fe[II,0]2+	-	381	0.0148
	L ⁺	353	
	Fe(L) ⁺	409	
Fe[III,1]2+	-	454	0.0070
	L ⁺	353	
	Fe(L) ₂ F ²⁺	391	
	Fe(L)F ⁺	428	
Fe[l,0]1+	-	762	0.0048
	LH⁺	354	
	Fe(L) ⁺	409	
	Fe(L)(gua) ⁺	547	
Fe[II,1]1+	-	907	0.0031
	Fe(L)F ⁺	428	
	$Fe(L)_2F^+$	781	
Fe[III,2]1+	-	1052	n/a
	n/o		

Cobalt

The species **Co[III,0]3+** shows the already known fragmentation pathway into L⁺ and $Co(L)^{2+}$. The ETD reduced species **Co[II,0]2+** again shows a very low abundance after fragmentation. The only fragments visible are L⁺, $Co(L)^+$ and **Co[III,0]3+**. The species with a counter ion **Co[III,1]2+** shows fragmentation and dissociation of the counter ion. But at low excitation amplitudes, a ligand moiety and fragmentation of the counter ion is observed. This channel decreases and vanishes completely at higher amplitudes. Here, fragmentation channels for **Co[III,0]3+** and **Co[II,0]2+** are opening (see Figure 23) and taking the lead. For the reduced species **Co[II,1]1+** only the fragment $Co(L)_2F^+$ is observed. No positively charged ligand is observed as a fragment,

so it is dissociated as a neutral molecule. The species **Co[III,2]1+** again shows L⁺, $Co(L)^+$, and $Co(L)F^+$ together with some fragments that couldn't be assigned, probably different fragmentation pathways of the ligand into small fragments. This also fits to the observation, that they start to appear at significantly higher excitation amplitudes and show a spacing of 14 m/z which could different numbers of CH₂ groups. The measurements of $[Co(dgpy)_2](BF_4)_3$ showed that the cobalt(III) species **Co[III,0]3+** has the highest stability and increasing m/z show lower $E_{COMz}^{50\%}$ values. One exception to this is **Co[III,1]1+**, which shows a lower stability than the species **Co[III,2]1+** with the higher m/z ratio. This, together with the fragments, are listed in Table 13.



Figure 23: CID appearance curves for all fragments of **Co[III,1]2+** and the sum of all fragments (TFY). At amplitudes of > 1 V **Co[III,0]3+** and **Co[II,0]2+** (gray squares and blue triangles) arises as the most intense fragment channels.

Table 13: Fragments observed and evaluated for the CID curves of the cobalt complex species. Unassigned fragments are missing here for clarity, but can be seen in the respective figures (see chapter 7).

Species	Fragment	m/z	$E_{COMz}^{50\%}$
Co[III,0]3+	-	255	0.0165
	Co(L) ²⁺	206	
	L ⁺	353	
Co[II,0]2+	-	383	0.0122
	L+	353	
	Co(L)+	413	
Co[III,1]2+	-	426	0.0116
	L ⁺	353	
	Co(L)2 ²⁺	383	
	Co(L) ⁺	413	
	$Co(L)F^+$	432	
Co[ll,1]1+	-	852	0.0032
	$Co(L)F^+$	432	
Co[III,2]1+	-	939	0.0051
	L ⁺	353	
	$Co(L)^+$	413	
	Co(L)F ⁺	432	

Nickel

[Ni(dgpy)₂](BF₄)₂ showed, similar to the other complexes, a low fragment intensity for the species **Ni[II,0]2+** (ca. 1% of precursor intensity), but still a low signal-to-noise ratio. The fragments, that could be observed, are L⁺ and Ni(L)⁺, but L⁺ has a very low relative intensity. The monocationic species **Ni[I,0]1+** shows only one fragment, Ni(L)⁺ which results from dissociation of neutral ligand. In the same way the species **Ni[II,1]1+** shows dissociation of neutral ligand but this time with and without a F⁻ attached to the resulting ion. In terms of stability, nickel follows the same trend as cobalt, with the 2+ species being the most stable and the reduced species being the most labile one. The respective appearance curves and $E_{COMz}^{50\%}$ values are shown in Figure 51.

Table 14: Fragments observed and evaluated for the CID curves of the nickel complex species. Unassigned fragments are missing here for clarity, but can be seen in the respective figures (see chapter 7).

Species	Fragment	m/z	$E_{COMz}^{50\%}$
Ni[II,0]2+	-	382	0.0148
	L ⁺	353	
	Ni(L) ⁺	413	
Ni[l,0]1+	-	764	0.0028
	Ni(L) ⁺	413	
Ni[II,1]1+	-	851	0.0036
	Ni(L) ⁺	413	
	Ni(L)F ⁺	432	

The first commonality in fragmentation pathways through all complexes is, that the species **M[II,0]2+** always has a low fragment intensity ($\leq 1\%$ of precursor intensity). This could be explained by dissociation neutral ligands leaving behind a M²⁺ ion, which has a lower m/z than the cut-off of the MS. Second is concerning the fragmentation of the counter ions:

- PF_6^- fragments leaving behind a F^- or sometimes remains bound
- BF₄⁻ dissociation intact or fragmentation leaving behind F⁻
- OTf⁻ remains bound, dissociation intact or fragmentation leaving behind F⁻, formal O⁻ or both

General fragmentation behavior

The pathways mentioned first are observed more often. It seems that BF_4^- has the weakest interaction between complex and counter ion, since it was never observed remaining bound to the precursor. PF_6^- shows typical fragmentation to F^- that was already observed in an earlier work. [122] OTf⁻ as the biggest counter ion shows all three possible pathways, thus the strength of its interactions towards the complex ion is probably in between the two others. Next to the counter ions also the dgpy ligand dissociates often from the complex ions. Usually, when the precursor ion has a charge of 2+ or 3+, dissociation of positively charged ligand is observed. With this also the remaining species has one charge less. There are only two exceptions to this: **Co[III,2]1+**

which simultaneously loses the weakly bound BF_4^- as well. Thus, the removed positive charge from the ligand gets compensated from the missing negative charge of the counter ion, fitting to the before mentioned statement. The second is **Mn[IV,3]1+** where also dgpy⁺ is observed as a fragment, but not the counter part, which should be something like [Mn(dgpy)](PF₆)_n⁺. This means that the complexes want to compensate the relatively high number of positive charges, which is supported by the electron donating properties of the ligand. [83, 123] With lower total charge (1+) usually the ligand remains bound or dissociates as a undetected neutral. This probably is caused by enough charge dissipation among the complex and the counter ions. Theoretical calculations most likely could verify or falsify this assumption.

Relative gas phase stability

In Figure 24 all $E_{COMz}^{50\%}$ values are shown, with colored boxes around the related species types, e.g., a purple box around all the **M[III,2]1+** species. It can be observed, that the relative gas phase stability decreases with decreasing m/z. Overall relative stability is similar for species with same oxidation- and charge number and counter ion amount, but the higher charged species show a bigger spread. **V[III,0]3+**, **Cr[III,0]3+** and **Mn[II,0]2+** show the three highest $E_{COMz}^{50\%}$ values, meaning the early transition metals have the highest stability. But other than the most stable species, no trend among one species type can be observed. An assumption would be, that the stability in gas phase of the investigated complexes is mostly dominated by size, i.e., number of possible fragmentation pathways. The smaller and higher charged species additionally probably possess a Coulomb barrier that needs to be overcome with higher collision energy for fragmentation.



Figure 24: $E_{COMz}^{50\%}$ values vs. the m/z of all CID curves. The same central metal ion always has the same colored symbol. Comparable species types are marked by the colored boxes around them. The two manganese(IV) species are without a designated boxes for clarity. A trend of decreasing stability with increasing m/z can be observed. Among the species types, no trend for the different metals is observed.

3.2.3 ultraviolet photodissociation

ultraviolet photodissociation spectra were measured for the complexes $[V(dgpy)_2](OTf)_3$, $[Cr(dgpy)_2](PF_6)_3$, $[Fe(dgpy)_2](PF_6)_2$, $[Co(dgpy)_2](BF_4)_3$, and $[Ni(dgpy)_2](BF_4)_2$. The chromium complex did not show photo induced fragmentation, therefore it will not be discussed here. The spectra were all measured in the same manner, from 220 - 400 nm in steps of 2 nm. At every point, the pulse energy was manually set to 1 μ J and mass spectra were recorded for 1 min per species. Afterwards all mass spectra were averaged and evaluated for all relevant fragments using equation (21). The target was to obtain gas phase UV/Vis spectra that can be compared to solution UV/Vis absorption spectra in literature. Furthermore, by analyzing the fragmentation behavior, information about the structure should be obtained. This can be compared to the results from the CID experiments. Additionally, power dependent spectra were measured at 265 and 320 nm from 0 to 2.5 and 0 to 5 μ J per pulse, respectively. This was done to find out more about the nature of the fragmentation process, whether it is a one photon or

a multi photon process. The resulting spectra were evaluated for the same fragments and plotted against the laser energy. All data together with their respective allometric fits are in the SI of this chapter (see 7.3), if not discussed here. In the following, the spectra will be discussed for each metal individually with comparisons to other metals, condensed phase measurements or theoretical results when suitable.

Vanadium

For the complex $[V(dgpy)_2](OTf)_3$ three UVPD spectra were obtained, for the species V[III,1]2+, V[II,1]1+, and V[III,2]1+ (Figure 25). The first observation is, that all these three species contain counter anions and are the less stable species regarding the CID experiments. All show absorption from 220 up to 370 nm including a strong band at about 250 nm and weaker bands at 290 and 310 nm. They don't have any fragments in common with each other, but show a very similar fragmentation compared to the respective CID measurements. The fragment specific spectra also do not show any differences from the total fragment yields (TFY) shown in Figure 61. The power dependent measurements shown in Figure 57 also show no clear photofragmentation for the species V[III,0]3+ and V[II,0]2+. The other three species instead, could be fitted with the allometric fit function and the exponent b is for all six measurements higher than 1. This hints towards the assumption, that a multiphoton process is present, meaning also these complexes need more energy than that of just one photon to fragment. Because of that, it could be that the energy absorbed even from multiple photons is still not enough to fragment the species without counter ions. In CID the two species without counter ions also were more stable, matching the result observed here.



Figure 25: UVPD spectra of the species V[III,1]2+, V[II,1]1+, and V[III,2]1+ with their respective arrow bars.

Iron

The species obtained from both solutions of the iron(II) complex and the iron(II) complex with ferrocenium added, show photo induced fragmentation up to almost 400 nm, with the exception that **Fe[II,0]2+** doesn't show significant fragmentation and **Fe[III,0]3+** only shows a spectrum with a low intensity. All other species show strong absorption at 220 nm, but differ at higher wavelengths. **Fe[I,0]1+** shows only one band at 240 nm and a weak shoulder-like feature at 305 nm, while **Fe[II,1]1+** has two bands, at 250 and 312 nm, which is slightly red shifted in comparison to the species without counter ion. The higher intensity, could be a result of the lower stability also observed in the CID experiments. To elucidate the nature of the spectra, fragment specific spectra can be used. All fragments of **Fe[I,0]1+** are probably resulting from decomposition of the ligand, giving a band at 240 nm. Important to note is, that this fragmentation of the ligand is not observed during the CID experiments. This could be a hint towards an electronic change of the ligand, i.e., a reduction caused by the additional electron of the ETD process. In CID there is the fragment where a guanidylpyridine moiety

is lost which was already interpreted as a sign for a reduced ligand, also in case of **Mn[II,0]1+**. **Fe[II,1]1+** shows two distinct fragments, $Fe(L)F^+$ with bands at 226, 240 and 312 nm and $Fe(L)_2F^+$ with no fragmentation at 220 nm and bands at 262 and 316 nm (compare Figure 26). Results from measurements in solution also show a strong band at 220 nm (Figure 27), while theoretical results for this range aren't available. [83] An assumption only based on the experimental results therefore would not be reliable. Secondary fragmentation because of the high flux at the low wavelength regime cannot be excluded. For the bands at higher wavelengths, mainly ILCT/LC bands are predicted. [83] Species **Fe[III,1]2+** doesn't show the band over 300 nm but only the shoulder, similar to **Fe[I,0]1+**. Compared to the condensed phase spectrum, Fe(III) fits a little bit better than the iron(II) species, but overall a good agreement can be observed. The fit of the power dependent spectra suggests a single photon process for all species, since the fit factor *b* is always about 1 or lower.



Figure 26: UVPD spectrum of the species **Fe[II,1]1+** with the fragment specific evaluation. The blue spectrum shows two bands at 262 and 316 nm.



Figure 27: Comparison of the measured gas phase UVPD spectra (top) and the solution UV/Vis spectra adapted from literature (bottom). The left graphs show the spectra of $[Fe(dgpy)_2](PF_6)_{2/3}$ and the right $[Co(dgpy)_2](BF_4)_3$.

Cobalt

For [Co(dgpy)₂](BF₄)₃ the most stable species Co[III,0]3+ and Co[II,0]2+ didn't show significant fragmentation, as well as the vanadium species without counter ion. While Co[III,1]2+ and Co[III,2]1+ show fragmentation up to about 330 nm, the spectrum of Co[II,1]1+ ends at about 380 nm. Similar to the spectra of iron are the absorption maxima at around 230 nm for all three species and another band at higher wavelengths (ca. 290 nm). For the band at 290 nm the complimentary fragment as in the iron case is responsible $(Co(L)_2F^+)$, but here, this fragment is detected from 250 - 340 nm as a very broad band. Since it is another counter ion (BF_4^-) instead of PF_6^- , a reasonable asssumption is, that the band could also refer to transitions which include the counter ion. Furthermore, this species has the least noisy spectrum, which also matches the result from CID, being the least stable species. Since it is already the least stable species, this could be the reason why the band assigned to the counter ion is visible here and not for the other two species even though they also have counter ions attached. Absorption spectra of the solution show the same band at about 220 nm, but another strong band at 320 nm, which could not be observed in gas phase (Figure 27). Theoretical results in literature predict mostly transitions centered on the ligand between 230 and 400 nm, but also show a strong band just below 300 nm as observed in gas phase. [81] The power dependent measurements suggest a multi photon process for **Co[III,1]2+** and **Co[III,2]1+** and a single photon process for **Co[II,1]1+**. This also matches the CID results, that the reduced species is the least stable.



Figure 28: UVPD spectrum of the species **Co[II,1]1+** with the fragment specific evaluation. Similar to **Fe[II,1]1+** the blue spectrum shows two redshifted bands not observed for the other fragments.

Nickel

The complex [Ni(dgpy)₂](BF₄)₂ shows some similarities to the before described complexes, even though it has a positive charge less. Here, the species **Ni[II,0]2+** doesn't show strong photon induced fragmentation and therefore no spectrum could be recorded. The species with the counter ion shows the typical strong fragmentation and the broad band at low wavelengths, followed from a decreasing signal, completely depleted at 360 nm. The reduced species, that was already the least stable, shows auto fragmentation (fragmentation without the laser). This reduces the significance of the observed spectral features, for example a strong peak at 300 nm, which results only from the correction of the laser energy at these wavelengths. Also, the signal not depleting to 0 over the whole spectrum is caused by this auto fragmentation. A manual subtraction of the background fragmentation was attempted, but resulted in just minimal change. The ions are probably already close to the dissociation limit and any photon is enough to surpass it. This is why the background correction doesn't work out as one would expect. Hence, any interpretation of this spectrum needs to be taken with caution. In literature there is no spectrum of the solution of the nickel complex in the same wavelength regime, thus no comparison is possible. [84]

Fragments observed for UVPD experiments have been compared to those of the CID measurements. Only in the case of **Fe[I,0]1+** more fragments were observed. These additional fragments are small fragmentation products of the ligand, that could not be assigned. This is probably caused by the high flux in the low wavelength regime around 220 nm. All other measurements showed the same or less fragments than CID. Thus, the fragments observed during the UVPD measurements are most likely a product of thermal fragmentation. This is also supported by the observation, that for all complexes the most stable species did not show photo fragmentation. Other than this, the received spectra of all complexes overall are similar too each other, with only small differences discussed before. The results from spectroscopy of the solution as well as theoretical results match the findings made in gas phase. The agreement is caused because in the measured regime here, the ligand is involved in almost all transitions (mostly LC or some LMCT). [81,83,84]

3.2.4 Ion-molecule reactions

For all complexes ion-molecule reactions with triethylamine (NEt₃) were measured, at a gas flow of 10% (TGC1 = 10) and a pulse duration of $t_{pulse} = 230 \ \mu s$. Compared with the publication of the manganese complex (see chapter 3.2), this corresponds to the "high amount of reactive gas added". Since the gas was added in a pulsed way, t_{trap} was varied from 0 to 250 ms. For the complexes [V(dgpy)₂](OTf)₃, [Cr(dgpy)₂](PF₆)₃, [Fe(dgpy)₂](PF₆)₂, [Co(dgpy)₂](BF₄)₃, and [Ni(dgpy)₂](BF₄)₂ no reaction was observed at all. Only for the in situ generated [Fe(dgpy)₂](PF₆)₃ complex, a small reactivity could be measured and only for the species **Fe[III,0]3+**. The product intensity was evaluated for the species **Fe[II,0]2+** and the NEt₃⁺ cation. No other products were observed when rechecking the recorded mass spectra. At 0 ms a small offset in product intensity of ca. 6% is observed and increases to ca. 14% at the maximum reaction time of 250 ms.

In comparison, manganese(III) (**Mn[III,0]3+**) showed a similar offset but only ca. 7% of product intensity at 250 ms reaction time, while manganese(IV) (**Mn[IV,2]2+**)



Figure 29: Relative intensities of the precursor ion **Fe[III,0]3+** and the reduced product complex species **Fe[II,0]2+** (left). Two mass spectra for the marked reaction times (10 and 200 ms) are given on the right.

showed an offset of 68% and 82% product intensity at 250 ms. These comparisons show, that the reaction rate of iron(III) towards NEt₃ is about the same as that of manganese(III), but much slower than manganese(IV). Different properties could play a role to explain this behavior. We see that the same oxidation number (III) at both metals show a similar reactivity, but given that non of the other complexes (V(III), Cr(III) or Co(III)) showed a reaction, this is not the most important factor. Same goes for the d-electron configuration. Since manganese(IV) is d³, manganese(III) is d⁴ and iron(III) is d^5 , other complexes with the same configuration should react at similar rates, e.g., (V(II), Cr(II/III)). But these did not show any reaction. Taking a look into the literature of the complexes, to be more precise, into the data of the cyclic voltammetric (CV) measurements, reveals a possible explanation. The redox potentials are listed in table Table 15. One can see, that with decreasing the redox potential, the product intensity also decreases. While manganese(IV) has a potential of $E^{ox/red} = +0.56$ V and shows a relative product intensity of 82% manganese(III) ($E^{ox/red} = -0.06$ V) only shows 7% of relative product intensity. A little outlier was observed for iron(III), but this should be in the error of the measurement or the density of the gas mixture. Therefore, one can expect, that also the excited states of the cobalt and manganese complexes would react very fast in the same ion-molecule reaction.

redox pair	$E^{ox/red}$ (V vs ferrocene)	$I_{rel}^{pro}(250 ms)$
<i>mer</i> -Mn ^{4+/3+}	+ 0.56	82%
<i>cis</i> -Mn ^{3+/2+}	- 0.06	7%
<i>mer</i> -Mn ^{3+/2+}	- 0.26	7%
<i>mer</i> -Fe ^{3+/2+}	- 0.65	14%
<i>mer</i> -Co ^{3+/2+}	- 0.98	0%
<i>cis</i> -V ^{3+/2+}	- 1.26	0%
<i>mer</i> -Mn* ^{4+/3+}	+ 2.0	n/a
<i>mer</i> -Co ^{*3+/2+}	+ 1.85	n/a

Table 15: Redox values of selected complexes and the relative intensity of the products of the reaction in gas phase towards NEt₃. The asterisk (*) marks electronically excited species. All electrochemical data taken from literature.

3.3 Future directions

3.3.1 Calibration of the neutral gas density

Since the density of the neutral gas inside the Paul trap is a crucial factor to obtain quantitative reaction rate constants, it is mandatory to get knowledge about the density. Direct pressure measurements inside the Paul trap are not possible, only in the surrounding chamber. This poses the problem that the sensitivity is way too low and small changes can not be monitored. Another problem is that the value from the cold cathode pressure meter is only measured with some delay and a typical error of around 30%. Therefore, another method to determine the neutral gas density is needed. By measuring different, literature known reactions with variable setting for pulse duration, gas flow of the PDI and trapping time, it should be possible to calculate the density. This was attempted by evaluating the measured pseudo first order kinetics in comparison to the bimolecular rate constant values taken from literature.

These experiments were already started during the student research internship of Noel Grimm, supervised by myself. In this study, we started measuring the same reactions as Parchomyk et al. [60] (equations (22) - (24)) and used their rate constants ($k_{2,Lit}$) as reference, while they used the results from Gronert et al. [124]

$$CF_3CH_2O^- + EtBr \longrightarrow CF_3CH_2OEt + Br^-$$
 (22)

$$CF_3CH_2O^- + iPrBr \longrightarrow CF_3CH_2OiPr + Br^-$$
 (23)

$$Br^{-} + MeI \longrightarrow MeBr + I^{-}$$
 (24)

The first experiments were performed by preparing the gas mixtures in the ratio of reactant gas:helium = 1:60, the reactant gas flow controller TGC1 was set to about 3.2% (which was the lowest reproducible value) and the pulse duration t_{pulse} was varied from 210 to 230 μ s in steps of 5 μ s. The respective ions were created by spraying solutions of CF₃CH₂OH (20 μ L) in methanol (1 mL) made basic by adding 10 μ L KOH solution or KBr (12 mg) in water (1 mL). For the reactions it was assumed that it is a pseudo first order reaction and the reactant and product intensities were accordingly fitted. The resulting fit value k_{eff} was then offset against the literature value to obtain an experimental rate constant $k_{2,Exp}$ (compare figure Figure 30). With this rate constant the density [R] could be calculated using eq. (25).

$$k_{2,Exp} = \frac{k_1}{[R]} \cdot C \tag{25}$$

In this equation the factor C is a correction factor for the ratio of the reactive gas and helium. The results suggest values for the neutral gas density inside the trap ranges from $2.6 - 7.9 \cdot 10^9 \cdot \text{ cm}^{-3}$ depending on pulse duration and gas type. These were only first experiments that showed that it is possible to calibrate our instrument for the reactant density.



Figure 30: First experimental results for the calibration of the reactant density inside the Paul trap by plotting the fit values k_{eff} against the literature known rate constants $k_{2,Lit}$. [125]

Further measurements of other reactions and with more variation in the settings are needed to get more reliable results. Of special interest to us, is a reaction with NEt₃. This is because it would be directly comparable to the measurements with the complexes in this work. Example reactions could be found in literature. Different groups measured rate constants for the reaction of NEt₃ with various protonated solvent clusters in a SIFT experiment. [126–128] One possible problem for the measurement of these reactions with the present ESI-MS could be the generation of the ionic clusters. Because of the nebulizer and especially the dry gas, which are usually to exclude solvent molecules, it stays questionable if these ions are accessible with the current setup. Some solvated metal ions like Na⁺, similar to the before mentioned literature could work. But this would need new kinetics measurements of the according reactions, to obtain reliable literature values.

3.3.2 IRMPD measurements at FELIX

In some cases, where the oxidation number of the central ion is unclear, e.g., **Mn[II,0]1+** or **Fe[I,0]1+** more spectroscopic methods can be helpful. Krämer et al. showed, spectroscopy in combination with quantum chemical calculations can provide information

about the oxidation states of the central metal ion or the ligand. [129] They also reduced a chromium(III) complex with one diazapyridinophane ligand. They were able to show, that the reduction from the Cr^{III} complex doesn't occur at the central ion. Instead the ligand, more specific, the pyridine moieties of the ligand get reduced. To further explore the nature of the reduced [M(dgpy)₂] complexes, we used the opportunity to visit the Free Electron Laser (FELIX) in Nijmegen in the late summer of 2024. Philipp Weber, Adela Ceman and I measured IRMPD spectra there. We recorded spectra for the six complex species from the [Mn(dgpy)₂](PF₆)₄ solution, the five species of the [Co(dgpy)₂](BF₄)₃ solution and two species of the solution of [Fe(dgpy)₂](PF₆)₃ (compare Table 16). We were not able to isolate the species from the [Fe(dgpy)₂](PF₆)₂ solution, therefore some are missing. Here, the first results of the experiments are shown. The measurements were performed at different attenuations of the IR beam given in dB, to provide more information and get better resolution for bands with large differences in fragmentation intensity.

Table 16: Available complex species of the complexes $[Mn(dgpy)_2](PF_6)_4$, $[Fe(dgpy)_2](PF_6)_2$, $[Fe(dgpy)_2](PF_6)_3$ and $[Co(dgpy)_2](BF_4)_3$ and the indication for which IRMPD spectra were obtained.

[Mn(dgpy) ₂](PF ₆) ₄		[Fe(dgpy) ₂](PF ₆) _{2/3}		[Co(dgpy) ₂](BF ₄) ₃	
Mn[III,0]3+	✓	Fe[III,0]3+	✓	Co[III,0]3+	✓
Mn[II,0]2+	✓	Fe[II,0]2+	✓	Co[II,0]2+	✓
Mn[IV,2]2+	✓	Fe[III,1]2+	X	Co[III,1]2+	✓
Mn[II,0]1+	✓	Fe[l,0]1+	X	Co[II,1]1+	✓
Mn[III,2]1+	✓	Fe[II,1]1+	X	Co[III,2]1+	✓
Mn[IV,3]1+	✓	Fe[III,2]1+	X		



Figure 31: Comparison of IRMPD spectra of the three complexes that were measured at FELIX. Always the **M[III,0]3+** species. No obvious spectral differences are visible. Attenuation is given in the legend for all spectra.

Figure 31 provides a comparison between all three measured complexes. For all central ions, always the species **M[III,0]3+** is shown. Since no big differences can be seen, the bands probably belong to the same vibrations in the respective complex species. Also in literature, the available ATR IR spectra show very similar bands in the same range. [78,83,84] Therefore, it is likely that these bands can be assigned mostly to the ligand.

Figure 32 shows a comparison of the six manganese species. Those were measured to get more information about oxidation states. The first observation is an additional broad band for the species with PF_6^- counter ions at about 860 cm⁻¹. This can directly be assigned. The gray vertical line marks a band at ca. 1633 cm⁻¹ that was only observed for **Mn[II,0]1+**. For this species, it was assumed that it is a manganese(II) central ion and a reduced ligand. This additional band strengthens our prior assumption which is based on the fragmentation pattern from CID. It should also be

noted, that in the ATR spectra measured in the group of Katja Heinze, the strong band about 1580 cm⁻¹ never shows a shoulder or another small band at higher wavenumbers. [78] This fits to the observations made in gas phase. The band of the counter ion (PF₆) at about 900 cm⁻¹ is slightly shifted towards higher wavenumbers in Figure 32 a). One possible explanation for this could be a stronger interaction between the anion and the higher charged manganese(IV) ion. Another difference can be seen at about 1400 - 1500 cm⁻¹. Here, are two bands, for which a change in intensity can be observed with decreasing oxidation state. For further interpretation of all spectra, reliable calculations are mandatory, and therefore no further statements can be made at this point. The spectra for the iron and cobalt complexes are in the appendix (Figure 65 and Figure 66).



Figure 32: Comparison of all IRMPD spectra of the manganese complex. a) and b) are manganese(IV), c) and d) are manganese(III), e) manganese(II) and f) is the species where a manganese(II) central ion with a reduced ligand was assumed. The gray vertical line marks an additonal band that is only observed for the potential reduced ligand species.

3.3.3 Electronically excited state ion-molecule reactions

As already mentioned in chapter 3.2.4, no ion-molecule reaction in gas phase towards NEt₃ was observed for the complexes with vanadium, chromium, cobalt or nickel as central ion. East et al. already showed an increased oxidative potential for the electronically excited state of the manganese(IV) complex in solution, that also oxidizes acetonitrile or benzene. [130] The redox values in table Table 15 also suggest that the excited state of the manganese complex should be more reactive. But also for the cobalt(III) complex it is reasonable to expect a reactivity towards NEt₃ in gas phase when electronically excited. Therefore, we already expanded the amaZon Speed,

where the UVPD experiments were performed, by a simple inlet for the reactive gas. A aluminum tank, filled with the gas mixture of NEt₃ and helium with a relative low pressure (ca. 1 bar) is connected to a needle valve and then directly into the helium line of the trap. By carefully opening the valve it is possible to insert the gas mixture continuously. With this setup we tried to measure reactions of the mentioned complexes while the laser is directed through the trap. These experiments are the most recent experiments and are part of the master's thesis of Adela Ceman, supervised by Philipp Weber and myself. It was not possible to even isolate the manganese(IV) species, probably because of reaction with the continuously added NEt₃ that seems to be faster than the isolation process. Anyways, it was possible to isolate the cobalt(III) species **Co[III,0]3+** and test the new setup. The first results are shown in Figure 33. They demonstrate that a reaction takes place, which is not the case while the laser pathway is blocked. These are the first experiments in this area in our group at the RPTU Kaiserslautern Landau and are a proof of principle experiment. It is planned to move the gas mixing unit and the control section described in chapter 2.1.4 from the amaZon ETD to the amaZon Speed to get more control over the inserted gas. Then it is needed to calibrate the inlet system again, but maybe therefore laser ionization reactions are also possible as additional guantification reactions.



Figure 33: First results on the ion-molecule reaction of the species **Co[III,0]3+** with NEt_3 inside of the Paul trap. The top graph (a) is without illumination, the bottom graph (b) with illumination i.e., excitation of the complex ions.
4.1 Ta⁺ and Nb⁺ + CO₂: intersystem crossing in ion–molecule reactions

Preamble

The following chapter consists of the publication "Ta⁺ and Nb⁺ + CO₂: intersystem crossing in ion–molecule reactions". The experimental data are a combination of crossed beam velocity map imaging (VMI) and selected-ion flow-tube (SIFT) measurements for the oxygen atom transfer reaction (OAT) of the niobium cation with CO₂. The study combines kinetics and dynamics for a full picture on a reaction. These reactions were the first two reactions investigated in Kaiserslautern with the VMI experiment. Niobium showed a very similar reaction pathway as the tantalum cation. [86] Therefore, in the publication are also comparisons to this reaction.

The acquisition of the experimental VMI data for both reactions were carried out by Marcel Meta and myself in the group of Jennifer Meyer at the RPTU Kaiserslautern-Landau in Kaiserslautern. The evaluation of the tantalum data was done by Marcel Meta, the evaluation of the niobium data by myself.

Tucker W. R. Lewis and Shaun G. Ard carried out the SIFT measurements and analyzed them together with Brendan C. Sweeny in the Air Force Research Laboratory at the Kirtland Air Force Base. Nicholas S. Shuman performed the statistical modeling, Milan Ončák the quantum chemical calculations and Yang Liu and Hua Guo the SVP simulations. The manuscript was prepared by Jennifer Meyer, Milan Ončák and Nicholas S. Shuman. I supported Jennifer Meyer in preparing the original manuscript.

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Ta^+ and $Nb^+ + CO_2$: intersystem crossing in Check for updates ion-molecule reactions* Cite this: Phys. Chem. Chem. Phys., Maximilian E. Huber, 🗈 ‡ª Tucker W. R. Lewis, ‡^b Marcel Meta, ២ a Shaun G. Ard, ^b Yang Liu,^c Brendan C. Sweeny,^b Hua Guo, ^b^c Milan Ončák, ^d Nicholas S. Shuman*^b and Jennifer Meyer ^b*^a

The reactions of Ta⁺ and Nb⁺ with CO₂ proceed only by a highly efficient oxygen atom transfer reaction to the respective oxide at room temperature in the gas phase. Although the product spin states are not determined, thermochemistry dictates that they must be different from ground state quintet Ta⁺ and Nb⁺, implying that intersystem crossing (ISC) has occurred. Recent reactive scattering experiments found dominant indirect dynamics for the reaction with Ta⁺ hinting at a bottleneck along the reaction path. The guestion on the nature of the bottleneck, whether it involves a crossing point or a transition state, could not be finally answered because theory located both close to each other. Here, we aim at shedding further light onto the impact of intersystem crossing on the reaction dynamics and ultimately the reactivity of transition metal ion reactions in the gas phase. We employ a combination of thermal kinetics for Ta⁺ and Nb⁺ with CO₂ using a selected-ion flow tube (SIFT) apparatus and differential scattering cross sections for Nb⁺ + CO₂ from crossed-beam velocity map imaging. The reaction with niobium again shows dominant indirect dynamics and in general very similar dynamics compared to Ta⁺ + CO₂. At thermal energies, both reactions show sub-collisional rate constants with small negative temperature dependencies. Experiments are complemented by high level quantum chemical calculations of the minimum energy pathway. Statistical modelling well-reproduces the experimental thermal rate constants, and suggests that the Nb⁺ reaction is rate-limited by the intersystem crossing at thermal energies.

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2024, 26, 8670

Introduction

In the gas phase, where confounding environmental factors can be eliminated, the mechanism of transition metal catalyzed reactions may often involve multi-state reactivity or in more specific cases two-state reactivity (TSR).^{1,2} That is, total electron spin is not conserved along the entirety of the reaction path. Even in cases where the reactant and product ground states conserve spin, the rate-limiting step may occur on a potential surface with a different multiplicity.2-4 Implicitly, these

reactions involve intersystem crossings (ISC). While a large body of work in both experiment and theory has advanced understanding, the processes are sufficiently complicated that basic questions even for (seemingly simple) ion-molecule reactions involving intersystem crossing remain challenging.

Whether or not a given reaction may involve intersystem crossing is generally determinable through chemical intuition, known thermochemistry, or quantum chemical calculations. However, whether an intersystem crossing will occur efficiently or if it will be rate-limiting is generally not readily determinable except through experiment. An exceptional computational effort for the FeO⁺ + H₂ system,^{4,5} a prototypical example of two-state reactivity,⁶ succeeded in matching experimental results7,8 showing that while an intersystem crossing was required for this spin-conserving reaction to occur at room temperature, the intersystem crossing was not rate-limiting. Similar efforts for larger systems are challenging and have not been reported. Commonly, a reaction pathway is calculated using density functional theory (DFT). Although the uncertainties in DFT energies for transition-metal containing systems are large, the structures along the pathway are mostly reliable. Where an intersystem crossing is apparent, a minimum energy

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crossing point (MECP) is located and the spin-orbit coupling at the crossing point is calculated and the Massey parameter⁹ estimated. Where the value is large, the intersystem crossing is assumed to be efficient and where the value is small, the intersystem crossing is assumed to be inefficient. This approach, while tractable, is fraught. The crossing is a multidimensional seam, and the spin-orbit coupling may vary widely along this seam such that evaluating the MECP alone is insufficient. An example of this failure is the Ti⁺ + CH₃OH reaction in which calculations¹⁰ predicted an inefficient intersystem crossing, but experiment¹¹ showed an efficient one. Despite issues such as this being reported in the literature for many years, practical concerns have resulted in simplifying assumptions that appear to be poor. Simply put, transition metal-containing catalytic reactions are complicated and insight into ISC in these systems remains limited for systems with few atoms, much less larger real world systems for which analogous processes have been observed.¹²⁻¹⁴ And even these small systems still pose challenges to experiment and theory alike.15,16

The reduction of CO₂ to CO is of obvious importance to science and society as a whole. The set of bare transition metal cations that reduce CO₂ at room temperature is defined almost entirely by thermochemistry; those metal cations with oxygen affinities greater than that of CO (5.45 eV) react with measurable efficiency, while those with smaller oxygen affinities do not.¹⁷ The exceptions are V⁺ and As⁺, which do not produce VO⁺ or AsO⁺ despite the processes being slightly exothermic. Both reactions (1) and (2) are exothermic and have been observed at room temperature. The reactivity has relevance to active sites of real-world catalysts employing Nb-containing materials for CO₂ reduction *via* electrocatalytic, thermocatalytic, and photocatalytic processes.¹⁸

 $Nb^+ + CO_2 \rightarrow NbO^+ + CO$ (1)

$$Ta^{+} + CO_{2} \rightarrow TaO^{+} + CO$$
 (2)

The kinetics of reaction (1) and (2) have been investigated previously both under thermal conditions at room temperature and as a function of collision energy. Bohme and co-workers found both reactions to be highly efficient at about a third of the capture rate.¹⁷ Sievers and Armentrout studied reaction (1) from ≈ 0.1 eV to 15 eV relative collision energy using a guided ion beam tandem mass spectrometer (GIB-MS) apparatus.¹⁹ Low energy collisions were consistent with a barrierless reaction and interpreted to be forming ground state triplet $\rm NbO^{+}.$ At higher energies, excited state product channels opened, including the spin-conserved reaction to form quintet NbO⁺. At the highest collision energies studied, minor channels forming NbCO⁺ and NbO₂⁺ were observed. The authors intuited a reaction pathway involving an intersystem crossing near the $[Nb^{+}(CO_2)]$ entrance well. That pathway is quite similar to pathway found by later DFT studies.^{20,21} For reaction (2), Schwarz and co-workers never directly measured the bi-molecular rate constant but inferred it to be capture limited or close to.²² Ion trap experiments also investigated the reaction of tantalum cluster cations with CO_2 , although the rate constants appear unphysically large.²³

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Recently, some of the present authors applied another experimental approach to the $Ta^+ + CO_2$ reaction by recording energy and angle differential cross sections in a reactive scattering experiment in combination with high level ab initio calculations.15 Differential cross sections give insight into the atomic level rearrangement during a reactive collision, thereby probing the dynamics of a reaction.²⁴⁻²⁷ If experiments are carried out under single collision conditions, energy and (angular) momentum conservation allow us to extract information on the molecular rearrangement during the reactive collision from the product ion velocity distribution. We can infer if a reaction is following direct dynamics, i.e. a reaction occurs upon impact, or if it is following a complex-mediated mechanism, which we refer to as indirect. Further, we can learn about how energy is redistributed between translational and internal degrees of freedom.²⁸⁻³¹ Weisshaar and co-workers were the first to investigate the dynamics of transition metal ions reacting with small molecules. However, their focus was on cobalt and nickel cations in reactions with C3-C4-hydrocarbons.32,33 The recent experiments were the first to take a look at the dynamics of the oxygen atom transfer reaction involving carbon dioxide.15 The TaO⁺ product was scattered predominantly isotropically at relative collision energies of up to 2 eV. The found indirect dynamics were surprising considering the limited number of states to dispose the available energy into. The collision energy combined with more than 2 eV of energy released in the reaction makes up a considerable amount of energy available to the reacting system. We reasoned that during the lifetime of the pre-reaction complex collision energy could be efficiently redistributed into internal energy. Once the bottleneck is passed, the now released energy is partitioned into product translation.³⁴ In the calculated reaction pathway, the MECP is located very close to the relevant transition state (see Fig. 1). Both the transition state and the minimum energy crossing point are submerged with respect to the free reactants and pose no thermodynamic barrier. Further the spin-orbit coupling efficiency for the heavy 5d elements is considered to be unity. Thus, the bottleneck seems to be dynamical in nature, or in other words a kinetic effect.

Similar reactions to the title reactions have been studied by some of the authors using a combination of temperature variable selected-ion flow tube (SIFT) experiments and statistical modelling.^{11,16,35,36} The rigorous treatment of the dynamics of transition metal ion molecule reaction is still not readily available. If the reaction, however, proceeds through a sufficiently long-lived intermediate, near complete ro-vibrational redistribution of energy can be assumed. That is, the reaction behaves statistical with respect to the isomerization and dissociation of the respective intermediate. Considering the correct treatment of angular momentum and reliable energetics, rate curves k(E,J)can be calculated. Bounds on the intersystem crossing lifetimes can be placed if experimental temperature dependent rates can be reproduced.³⁶ The Ti⁺ + CO₂ reaction displayed an unusual combination of low efficiency and small negative temperature

Phys. Chem. Chem. Phys., 2024, 26, 8670-8680 | 8671

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Fig. 1 Potential energy profile along the suggested reaction coordinate for NbO⁺ + CO₂ \rightarrow NbO⁺ + CO Structures of the stationary points along the minimum energy path are given, i.e for the pre-reaction and post-reaction complexes as well the transition states, for the quintet surface (green) and triplet (orange) surface (Nb = light blue, carbon = black, oxygen = red; structural data can be found in the ESI⁺). The orange coloured energy profile refers to the quintet state, while the energy profile of the triplet state is depicted in green. The reaction of Ta⁺ + CO₂ is given as comparison to Nb⁺ + CO in the same colour code but in shaded colours. Both energy profiles are referenced to ⁵M⁺ + CO₂. M is used whenever the energies of the respective states for Nb and Ta are close to indistinguishable from each other. Kinematic cut-offs are calculated using the presented reaction energies for the reaction of ⁵Nb⁺ to ³Nb⁺ to ³Nb0⁺ (*E*(⁵Nb⁺) = -1.99 eV and *E*(³Nb⁺) = -2.41 eV). The potential energy profile for TaO⁺ + CO₂ is given as comparison.¹⁵ The inset shows the structures energies of the crossing points (CPs) from quintet to triplet and between Ta(dark blue) and Nb (light blue). All energies are relative to the structures) are calculated using the CCSD(T) method at the geometries optimized with MP2 and with CCSD. The aug-cc-pVTZ basis set was used for C, O, the ECP28MDF_AVTZ basis set for Nb, and ECP60MDF_AVTZ for Ta (see the Methods for details). The crossing points were optimized at the CCSD level.

dependence.¹⁶ Statistical modelling reproduced the results well assuming that an intersystem crossing was rate limiting and did not reproduce the data acceptably assuming instead that a transition state was rate limiting. In this picture, the intersystem crossing was treated as having a characteristic lifetime to a crossing occurring, in competition with possible isomerization or dissociation. The modeling fit the data assuming this lifetime was on the order of 10^{-7} s, with about an order of magnitude uncertainty. The same methodology showed very different intersystem crossing lifetimes in the reactions of Ti⁺ + O₂ and Ti⁺ + N₂O, varying from microseconds to sub-picoseconds.¹⁶

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In the present study, we combine experimental and theoretical efforts for a deeper insight into the behaviour of the possible statistical behaviour of the oxygen atom transfer reaction between Ta^+ and carbon dioxide and its lighter homologue niobium Nb⁺. Energetics along the reaction pathway have been calculated at the coupled cluster level of theory. The results give reliable input for the evaluation of energy partitioning in case of experimental differential cross sections and as input for the statistical modelling of the reaction rate and intersystem crossing rates. The results will be interpreted with respect to the possible and most probable bottleneck along the reaction pathway.

Methods

Experiment

Crossed beam velocity map imaging. Niobium cations Nb^+ are crossed with a molecular beam of CO_2 under single collision conditions in the interaction region of a velocity map imaging spectrometer. The experimental set-up has been

8672 | Phys. Chem. Chem. Phys., 2024, 26, 8670-8680

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described in detail previously.¹⁵ Only a brief explanation will be given here. Ions are formed in a laser vaporization source37,38 by focusing the 2nd harmonic of a Nd:YAG laser (Innolas Spit-Light, 532 nm, 20 Hz, \approx 4 mJ per pulse) onto a rotating niobium target (Alfa Aesar, 99.97%). The generated plasma is swept up by a synchronized helium pulse (8 bar He, 40 µs; AirLiquide, alphagaz 1) oriented perpendicularly to the laser propagation direction. The source is operated such that Nb⁺ cations are formed and cluster formation is suppressed. The ions undergo on the order of 10⁴ collisions with helium before entering the high vacuum region of the source chamber which is insufficient to efficiently quench possible electronically excited states. For tantalum, we estimated an upper limit of electronically excited triplet states at 20% in accordance with estimations of comparable ion sources.^{39,40} The laser vaporization source is oriented in line with the velocity map imaging (VMI) spectrometer.^{41,42} Once the ions are transferred into the interaction region of the VMI, the ion beam is crossed at 150° with a synchronized molecular beam of pure CO2 (AirLiquide, 99.995%) from a home-built piezo-electric valve. Product ions are mapped onto a position and time sensitive detector unit perpendicular to the scattering plane using velocity map imaging conditions.⁴³ We operate the VMI in a pulsed mode, *i.e.* the electrodes of the VMI spectrometer are switched from an off-set voltage to imaging settings about a 1 µs after the mean of ion and neutral beams pass the interaction region. The combination of a multi-channel plate stack, phosphor screen, and camera records the velocity components in the scattering plane, here denoted (v_x, v_y) . The multi-channel plates are switched to single-ion counting conditions once the arrival time of the reactant ion beam is passed. A photo-multiplier tube records the arrival time of the ions, which contains information of the velocity along the z-direction. We can recover the 3D Newton sphere due to the cylindrical symmetry of the scattering geometry in the center-of-mass frame. We display the resulting 2D histograms weighted by the radial velocity v_r to be better comparable to sliced images.^{41,42,44} The relative collision energy is adjusted by varying the potential off-set of the ion source relative to the DC off-set applied to the velocity map imaging lens stack. Relative collision energies were chosen to compare to the experiments of $Ta^+ + CO_2$. Efforts were made to reach energies for which Sievers and Armentrout found the opening of new product states¹⁹ but the current experimental configuration did not allow lower or higher collision energies than the presented. On the lower limit, reliable control of the ion beam could no longer be achieved and at the higher limit the acceptance of the detector was reached. Scaling of the magnification settings would have resulted in additional challenges due to background from the ion beam. Both reactant beams are characterized by 2D velocity map imaging, in case of CO2 after electron impact ionization. The 1σ -error of the collision energies due to velocity and angular spread of both input beams is between 65 to 140 meV for the presented experiments. Errors of the product ion velocity and respective energy distributions are obtained from Gaussian error propagation.⁴

Selected-ion flow tube. The variable-ion source, temperatureadjustable, selected-ion flow tube (VISTA-SIFT) and laser

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vaporization (LaVa) ion source used here have been described in detail previously.⁴⁵ Briefly, a rotating, translating 1/4" diameter tantalum (ESPI Metals, 99.9%) or niobium rod (ESPI Metals, 99.9%) was vaporized and ionized using the $2^{\rm nd}$ harmonic of a Nd:YAG laser (Litron) operating at 100 Hz. The ions were entrained in an expansion of argon (Matheson, 99.999%) from a high-speed pulsed valve (Parker Iota One) also operated at 100 Hz. Ions were transported using a series of quadrupolar ion guides to a quadrupole mass filter. Mass selected ions were transported using another series of quadrupolar ion guides and injected into a stainless steel, 1 m long, 7 cm diameter reaction flow tube via a Venturi inlet. The ions were entrained into a flow of helium (Matheson, 99.999%), typically 12 std. L min⁻¹ and 0.35 torr. The temperature of the flow tube was variable from 100-700 K using either liquid nitrogen pulsed through copper tubing braised to the outer wall or resistive heating elements wrapped around the exterior. CO2 was added through a finger inlet 55 cm prior to the terminus of the flow tube *via* a mass flow meter (MKS) at a variable flow from 0.1 to 10 std. cm³ min¹. A typical reaction time was 2.5 ms. At the end of the flow tube, the bulk of the gas was removed using a Roots-style pump (Leybold) while the gas along the centre axis was sampled through a 4 mm aperture in a rounded, carbon-coated nosecone into a higher vacuum region. The ions were transported using a quadrupolar ion guide to the entrance of an orthogonallyaccelerated time-of-flight mass spectrometer (Jordan TOF). Reactant and product ion abundances were monitored as a function of the neutral gas concentration. The mass-selected ions underwent 10⁴-10⁵ collisions with the buffer gas in the flow tube prior to introduction of the neutral reactant. For polyatomic species, this is sufficient to reliably quench to a thermal distribution at the temperature of the flow tube walls. For monatomic species, as was the case here, thermalization is less certain. Both Nb⁺ and Ta⁺ have a number of low-lying states.⁴⁶ While the experiment did not directly probe the state of the reactant ions, several observations suggest that the distributions were largely thermal. In all cases, the decay of the primary ion was well-described by a single exponential. The measured kinetics did not vary upon introducing $N_{\rm 2}$ or CO at $10^{13}\ cm^{-3}$ to the flow tube. The measured kinetics did not vary with varying ion source conditions and were consistent from day-to-day.

Theory

Quantum chemical calculations. Local minima and transition states were optimized using the coupled cluster singles and doubles (CCSD) method along with the aug-cc-pVTZ basis set on carbon and oxygen and the ECP28MDF_AVTZ basis set on Nb.⁴⁷ To obtain more reliable energies, singe-point recalculation with non-iteratively included triplets, CCSD(T), was performed. The zero-point energy was included as calculated at the CCSD level. Due to convergence issues, the transition state in triplet spin multiplicity was optimized using Møller-Plesset perturbation theory, MP2 (Table S4, ESI† shows that the optimization method does not affect the relative energy considerably). We used the EasyMECP program⁴⁸ to localize the

Phys. Chem. Chem. Phys., 2024, 26, 8670-8680 | 8673

PCCP

View Article Online

Paper

triplet/quintet minimum energy crossing point. While we succeeded to optimize the crossing point at the B3LYP/aug-cc-pVTZ level (with the gap of 17 kJ mol⁻¹ after CCSD(T) recalculation, lying 9.9 kJ mol⁻¹ below the entrance channel), the search for the triplet/quintet minimum energy at the CCSD level did not converge. Still, we localized a point with the 0.5 kJ mol⁻¹ energy difference between quintet and triplet surfaces at the CCSD/aug-cc-pVTZ level. This gap increases to 14 kJ mol⁻¹ after CCSD(T) single-point recalculation, the point lies below the energy of the entrance channel at -6.6 kJ mol⁻¹. Wave function stabilization was performed prior to each structure optimization. All calculations were performed in the Gaussian software package.⁴⁹

Statistical modeling. Full details of the statistical modeling are provided elsewhere.16,36 Briefly, a reaction path was assumed defined by stationary points from the quantum chemical calculations. Unimolecular rate curves for possible isomerizations k(E,J)were calculated as well as for possible dissociations using the simplified statistical adiabatic channel model (SSACM). Initial conditions, reactant vibrations, rotations, relative kinetic energy, and impact parameter were selected stochastically from thermal distributions defined by a single temperature. The long-range potential was defined solely by electrostatic interactions. For each trial, if the kinetic energy exceeded the centrifugal barrier, a complex was assumed to be formed otherwise no reaction was assumed; this reproduced the Langevin-Gioumousis-Stevenson (LGS) capture rate constant.^{50,51} For complex-forming reactions, the system evolved through competition of dissociation and isomerization with probabilities equal to the relative specific k(E,J). An ISC was treated as connecting two stationary points via a transition probability defined by an energy- and angular momentum-independent lifetime competing with relevant isomerization or dissociation. A sufficient number of trials, generally $10^3 - 10^6$, were completed to reduce the statistical scatter to less than 1% in the rate constant.

Sudden vector projection (SVP). The Sudden Vector Projection (SVP) model^{52,53} is based on the premise that the ability of a reactant mode in promoting the reaction is proportional to its coupling with the reaction coordinate at a transition state. Hence, the SVP values result from projection of the product modes onto the saddle point, respectively. They are unitless and range between 0 and 1. This assumption is reasonable for direct reactions in which the collision time is significantly shorter than that needed for intramolecular vibrational energy redistribution (IVR) of the reactants. The SVP can be considered as a generalization of the Polanyi rules for atom–diatom reactions,²⁹ which attribute the relative ability of reactant vibrational and translational excitation to enhance reactivity to the location of the transition state along the reaction path.

Results

Minimum energy pathway

The minimum energy reaction pathway for Nb⁺ + CO₂ \rightarrow NbO⁺ + CO shows all features typical for an exothermic gas phase ion molecule reaction. The pre-reaction complex [MCO₂]⁺ is based

on electrostatic interactions with the charge quadrupole interaction being the leading term.^{21,54,55} The permanent negative quadrupole moment of CO2 leads to a linear structure of the pre-reaction complex in both spin states (see Fig. 1). That the interaction is almost purely electrostatic can also be seen by the fact that the well-depth of $[NbCO_2^+]$ is the same as for [TaCO₂]⁺. The transition state on the quintet surface is characterized by an almost fully cleaved C-O bond and pre-formed products NbO⁺ and CO. It is a typical late transition state and endothermic by about one electron volt. As is well known, the reaction is facile at ambient temperatures.^{17,19} The reaction starts on the quintet ground state and moves from there via intersystem crossing to the triplet state which features a much lower barrier compared to the quintet surface. The saddle point on the triplet surface is close in energy to the free ground-state reactants and located earlier along the reaction pathway. The CO_2 is bent by $\approx 15^\circ$. All this is in agreement with the Hammond postulate which states that such significant differences in barrier heights are only possible if the structures in both spin configurations are significantly different from each other.56 This behaviour is well-known for transition metal mediated reactions and generally referred to as multi-state reactivity or two-state reactivity.² Recently, it has also been identified for metal-free systems with radical character.⁵⁷ In the present case, reaction (1) bypasses both transition states because the minimum energy crossing point is located after the triplet transition state and the quintet transition state is never reached. The deep minimum of the post-reaction complex is reached which can be characterized by the coordination of a CO molecule to the niobium oxide cation NbO⁺. The minimum energy pathway for the oxygen atom transfer reaction for Ta⁺ + CO_2 is given as comparison¹⁵ in Fig. 1. Structures of stationary points are shown in Fig. 1. Only minimal differences can be observed for tantalum and niobium (for structural data please see Table S3. ESI[†]).

The minimum energy pathway and the stationary points including crossing points have been investigated before with density functional theory.^{19,20} The structures and general features of the surface agree with the known data from the literature. However, for a reliable analysis of the energy partitioning, we rely on the energies of the stationary points from theory which are prone to fluctuations depending on choice of parameters using DFT. Here, we present the stationary points calculated at coupled cluster CCSD(T) level. Our calculated reaction energy of -1.99 eV compares reasonably well with the experimental value of -1.68 eV from guided ion beam experiments.¹⁹ The energy needed to release the CO from the post-reaction complex [ONbCO]⁺ compares equally well to experimental values derived from collision induced dissociation energy of [ONbCO]⁺ \rightarrow NbO⁺ + CO which gave a dissociation energy of about 1 eV.¹⁹

Differential cross sections Nb⁺ + CO₂

Reactive scattering experiments have been performed for the niobium cation Nb^+ and CO_2 forming NbO^+ to record experimental differential cross sections which encode information on the underlying dynamics (see Fig. 2). Experiments have been

8674 | Phys. Chem. Chem. Phys., 2024, 26, 8670-8680

View Article Online

conducted at 1.3 eV and 2.2 eV relative collision energy. At both energies, NbO⁺ ions are predominantly isotropically scattered around the center-of-mass at small velocities well away from the respective kinematic cut-offs. The kinematic cut-off is calculated as the maximum possible product ion velocity considering energy and momentum conservation. Ions with smaller velocities indicate that a fraction of the available energy is partitioned into ro-vibrational excitation of the molecular products NbO⁺ and CO. This agrees with the isotropic scattering which is a signature for a complex mediated mechanism in which an interaction complex between the reactants lives for several rotational periods before dissociating into products.28,31 During this time transfer of energy from translational to internal degrees of freedoms is possible. In other words, the complex lifetime is much longer than the timescale of intromolecular vibrational energy redistribution (IVR). We want to point out two things. First, that that we work under single collision conditions and no energy can be dissipated to the environment. Secondly, that the reaction is exothermic by about 2 eV which makes more than 3 eV available to the



Fig. 2 Differential cross sections for $Nb^+ + CO_2$ (a) and (b) product ion $\rm NbO^+$ velocity distributions at $E_{\rm rel}$ = 1.3 eV and 2.2 eV relative collision energy. Distributions are normalized relative to the bin of highest intensity. Kinematic cut-offs indicating the maximum possible energy partitioned into product translation are given by the green (guintet ground state) and orange (triplet excited state) rings. Product ions are mostly scattered isotropically around the center-of-mass with some asymmetry towards the backward plane at low collision energy and towards the forward plane at 2.2 eV. The Newton diagram at the top illustrates the relative orientation of the reactant beams in the center-of-mass frame used to display the velocity distributions. (c) and (d) Normalized integrated angular distributions. The area of the histograms is set to one. The gray histograms show the corresponding distributions for the reaction with tantalum. For $\theta\,\leq\,$ 155° (cos $\theta \leq 0.8$) incomplete background subtraction leads to artifacts (pink shaded areas). The dashed pink lines (a) and (b) indicate the cuts used to calculate product energy distributions (see Methods). Angular integrated distributions for $Ta^+ + CO_2 \rightarrow TaO^+ + CO$ adapted from ref. 15

reaction. The integrated angular distributions reveal slight asymmetries to the scattering distributions (Fig. 2c and d). While the NbO⁺ ions show some more intensity in the backward hemisphere at E_{rel} = 1.3 eV, at E_{rel} = 2.2 eV the trend shifts towards the forward hemisphere. The relative orientation of the reactant beams in the center-of-mass frame are illustrated by the Newton diagram at the top of Fig. 2. The forward hemisphere is defined by the initial direction of the neutral beam and corresponds to a scattering angle of $\theta = 0^{\circ}-90^{\circ}$ and the backward hemisphere accordingly to $\theta = 90^{\circ}-180^{\circ}$, *i.e.*, the initial direction of the ion beam. In the present case, the ion Nb^+ (93 amu) is heavier than the neutral reactant CO_2 (44 amu). A direct rebound leads to a momentum reversal, meaning the niobium turns around. Thus, scattering into the forward hemisphere as seen at 2.2 eV indicates a direct rebound. At both energies, the scattering angles close to θ = 180 $^{\circ}$ are obstructed due to signal from the ion beam leaking into the scattering signature. This is caused by the close arrival times of reactant and product ions at the detector and by the center-of-mass being located close to the ion beam incident position on the detector. The angular distribution for reaction (2) is added as a grey line in Fig. 2c and d for comparable relative collision energies of 1.4 eV and 2.0 eV15 for a direct comparison with the distribution for reaction (1). Both reactions show very similar angular distributions. The velocity cut used for evaluation of the energy distributions is indicated by the pink dashed lines. The cut in absolute velocity was chosen as the kinematic cut-off plus the 2 σ -error of the product ion velocity from error propagation of the reactant beam velocity and angular spreads.⁴¹ The integrated energy distributions of the full scattering range (θ = 0° -180°) together with the 1 σ -error is given in Fig. S1 (ESI†). NbO⁺ ions are scattered well within the kinematic cut-off of the ground state reaction and no significant product ion flux is seen outside the 2σ -error. In case of direct dynamics leading to scattering close to the kinematic cut-off, energy conservation arguments can be used for insight into the reactant beam composition. Due to the highly indirect nature of the reaction, we cannot conclude if NbO⁺ ions formed in reactions of electronically excited Nb⁺ ions. In case of Nb⁺ in its electronically excited triplet reacting, the reaction is spin conserving and follows the typical pathway of an exothermic ion-molecule reaction in the gas phase. At the investigated collision energies, we would expect direct dynamics to be dominant, i.e., a significantly more anisotropic angular distribution and less energy partitioning into internal excitation of the products.

Here, we show the fractions of the total energy available to the reaction which is partitioned into internal energy (Fig. 3a) and product ion translation (Fig. 3b). The total available energy is calculated as the sum of the relative collision energy $E_{\rm rel}$ and the energy of the triplet products with respect to the quintet reactants, ${}^{5}Nb^{+} + CO_{2} \rightarrow {}^{3}NbO^{+} + CO$. The relative energy partitioning between internal and translational energy is almost the same at both investigated collision energies, meaning that additional collision energy is mostly partitioned into internal excitation of either NbO⁺ or CO. We find a mean value of $f_{\rm int} \approx 0.6$. Energy distributions in absolute units of energy

Phys. Chem. Chem. Phys., 2024, 26, 8670-8680 | 8675

PCCP



Fig. 3 Comparison of energy partitioning for reactions with niobium and tantalum. Relative fractions of energy partitioned into (a) internal excitation of the products $MO^+ + CO$ and (b) product ion MO^+ translation are given. The energy scale is set relative to the total available energy for each respective reaction. Histograms are each normalized to an area of one. Histograms in absolute energy scale including errors for the respective energy distributions from Gaussian error propagation are given in Fig. S1 (ESI†). Integrated energy distributions for Ta⁺ + CO₂ \rightarrow TaO⁺ + CO addapted from ref. 15.

(here eV) are given in Fig. S1 (ESI[†]) including errors to the product ion energies. A direct comparison of both investigated collision energies is plotted in Fig. S2 (ESI[†]). The distributions for the reaction with tantalum are drawn as dashed lines as direct comparison. Similar to the angular distributions, the energy distributions are highly comparable. Slightly more energy seems to be channelled into product ion translation in case of niobium but within the experimental error we cannot conclude this to be significant.

Both reactions encounter a bottleneck along the reaction pathway which leads to trapping with the associated life-time to redistribute energy. Considering the near constant kinetic energy release we reasoned in case of tantalum that the trapping happens on the reactant side and once the bottleneck is passed the reaction goes downhill and the products accelerate flying away from each other. This result is surprising because we have very exothermic four atom reactions combined with a reaction in which only a single atom is transferred. In case of direct dynamics, one could envision a classic heavy M^+ – light O – heavy CO scenario as for example described by Polanyi.²⁹ However, our experimental differential cross sections give evidence for highly indirect dynamics. Therefore, we took a closer look at the thermal rate constants for the title reactions.

Thermal rate constants $k(T) M^+ + CO_2 (M = Nb, Ta)$

Representative mass spectra and kinetics from the SIFT experiment are available in the ESI⁺ (Fig. S4 and S6). Ta⁺ reacted to form only TaO⁺, which in turn reacted rapidly with CO₂ to yield TaO₂⁺. TaO₂⁺ associated with CO₂ to yield TaO₂⁺(CO₂)_{1–3}. Nb⁺ reacts similarly, but also producing small amounts of NbO⁺(CO₂)_{1–3}. Details of the sequential chemistry beyond reactions (1) and (2) are provided in the ESI.⁺ The rate constants for reactions (1) and (2) from 200 to 600 K are shown in Fig. 4. Both reactions proceed at a significant fraction of the Langevin capture rate constant (Nb⁺: 6.8×10^{-10} cm³ s⁻¹; Ta⁺: 6.3×10^{-10} cm³ s⁻¹) with mild negative temperature dependence for each one. Over the measured range, the rate constants are well represented by ($k_{Ta^+CO_2} = 4.5 \pm 1.0 \times$



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Fig. 4 Thermal rate constants derived from the SIFT measurements for reactions (1) (Nb⁺ + CO₂, red circles) and (2) (Ta⁺ + CO₂, blue squares). Curves are best-fits from statistical modelling (see text) assuming the reactions are rate-limited either by the transition state (dashed) or ISC (solid). Thin lines are Langevin–Gioumousis–Stevenson (LGS) capture rate constants.^{50,51}

 $10^{-10} \times (T/300)^{-0.2\pm0.1} \text{ cm}^3 \text{ s}^{-1}$, $k_{\text{Nb}^++\text{CO}_2} = 3.4 \pm 0.9 \times 10^{-10} \times (T/300)^{-0.7\pm0.2} \text{ cm}^3 \text{ s}^{-1}$).

In previous work, a statistical modeling approach was applied to the $Ti^+ + CO_2 \rightarrow TiO^+ + CO$ reaction.¹⁶ As for the systems here, the calculated minimum energy pathway is ambiguous as to whether a necessary intersystem crossing affects the kinetics. The measured $Ti^+ + CO_2$ rate constants were smaller than for the Nb⁺ and Ta⁺ reactions reported here, and had a steeper negative temperature dependence, $k_{Ti^++CO_2} = 5.5 \pm 1.3 \times 10^{-11} \times (T/300)^{-1.1\pm0.2}$ cm³ s⁻¹. The experimental results were well-reproduced by assuming that the ISC was rate-limiting, while no reasonable fit to the data was possible assuming that the transition state was rate limiting. In the model, the ISC was not treated explicitly, but instead defined by an average lifetime to the crossing occurring, with that lifetime adjusted to fit the experimental data. For $Ti^+ + CO_2$, that lifetime was on the order of 10^{-7} s.

For a statistical approach to be applicable, the initial complex must be sufficiently long-lived to allow for IVR to be near complete. Typical IVR timescales for small molecules are on the order of pico seconds but can be significantly longer. The calculated rate curves of the dissociation of the entrance complex back to reactants assuming phase-space behavior are shown in Fig. 5. At energies 1 to 2 eV above threshold, the rate constants are no larger than 10^{10} s⁻¹, indicating that a statistical treatment may be appropriate. The rate constants for dissociation into the free products from the post-reaction wells in both reactions are much larger (Fig. S7, ESI[†]) and should not occur statistically; however, this should not affect treatment of



Fig. 5 Calculated unimolecular rate curves for dissociation of (A) 5 Nb⁺(CO₂) and (B) 5 Ta⁺(CO₂) as a function of the internal energy of the complex for J = 0, 50, 100, 150, and 200.

the earlier, rate-limiting step. It is likely that the statistical model can reproduce the general aspects of the kinetics, although non-statistical elements may well be present.

The best-fits from statistical modeling for both systems are shown in Fig. 4. Scenarios were investigated assuming either the triplet transition state was rate-limiting, an ISC was ratelimiting, or both features contributed. The curves shown are the limiting cases. The calculated energetics for the complexes and the transition states relative to the separated reactants were

Table 1 Best-fit parameters for the reactions of M⁺ + CO₂ \rightarrow MO⁺ + CO determined using statistical modelling under the scenarios described in the text. Energies are relative to separated ground-state reactants. *Ab initio* values for Ta⁺ + CO₂ from ref. 15

	Transition state er				
		Ab initio			
	Statistical model	Singlet	Triplet	Quintet	Lifetime (s)
Ti ¹⁶ Nb		0.15	± 0.00	0.84	$\approx 10^{-7}$ 10^{-8}
Та	$-0.2\pm$ 0.1	-0.07	-0.34	0.53	$< 10^{-9}$

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varied along with the ISC lifetime. For reaction (2), Ta⁺ + CO₂, either scenario (or a combination) provide good fits to the experimental data, with best fit values shown in Table 1. For reaction (1), Nb⁺ + CO₂, an acceptable fit to the data is only achieved by assuming the ISC is rate-limiting. For reaction (2), the data are well fit assuming the triplet TS is -0.2 ± 0.1 eV below reactants (or more negative if ISC also contributes), in reasonable agreement with the calculated value. Alternatively, if the reaction is controlled by ISC alone, the data are fit by an average lifetime to a crossing of $\approx 10^{-9}$ s, which can be viewed as an upper limit if the TS also contributes. In comparison, the data for reaction (1), Nb⁺ + CO₂, are well fit assuming an average ISC lifetime of 10^{-8} s.

The thermal reactions are distinct from the beam measurements in that the spin-conserved products are always energetically prohibited. Additionally, the calculated spin-conserving quintet transition state is also energetically inaccessible. Singlet and triplet product states are accessible, although the experiment does not probe the nature of those states.

The 300 K rate constants reported here for reactions (1) and (2) $(3.1 \pm 0.9 \times 10^{10} \text{ cm}^3 \text{ s}^{-1} \text{ and } 4.5 \pm 1.0 \times 10^{10} \text{ cm}^3 \text{ s}^{-1},$ respectively) are \approx 70-90% larger than those reported previously by Bohme and co-workers (1.8 \pm 0.6 \times 10^{10} cm 3 s^{-1} and 2.4 \pm 0.8 \times 10 10 cm 3 s $^{-1}$). 17 This is a larger disagreement than is typical between the experiments. That the reactant ions are monoatomic and have low-lying electronic states causes concern that the reactant state distribution is non-thermal in one or both experiments, but the underlying cause of the discrepancy is not certain. For reaction (1), both the literature SIFT value and the present results are more efficient (0.26 and 0.47, respectively) relative to the LGS capture rate^{50,51} than a guided ion beam measurement extrapolated to 300 K translational energy (0.12).¹⁹ The temperature dependence of reaction (1), $T^{-0.7\pm0.2}$, is in reasonable agreement with the translational energy dependence previously reported for the reaction of $E^{-1.0}$ \pm 0.1,¹⁹ where T^x is equivalent to $E^{x-0.5}$. Surprisingly, Armentrout has not published on reaction (2).

Discussion

Both reactions (1) and (2) occur at a substantial fraction of the LGS capture rate and show mild negative temperature dependencies in the rate constants, common occurrences for exothermic ion-molecule reactions. However, the observed reaction dynamics are dominated by indirect dynamics with a high fraction of ro-vibrational excitation of MO^+ and/or CO. Additional collision energy seems to be almost exclusively partitioned into the internal excitation leading to a near constant kinetic energy release. This energy release is close to the energy difference between the entrance channel complex and the free products. A sufficiently long-lived entrance channel complex as is the case here, provides the explanation for both experimental observations because the long lifetime allows for efficient redistribution of energy within the entrance channel complex followed by a fixed amount of energy being released as

Phys. Chem. Chem. Phys., 2024, 26, 8670-8680 | 8677

PCCP

product kinetic energy. The negative temperature dependence of the rate constant arises from competition between an entropically favoured dissociation back to reactants and an energetically favoured isomerization to the product well. Statistical treatment is often successful at quantitatively reproducing this effect by treating calculated transition state energies, which may have uncertainties on the order of hundreds of meV, as adjustable parameters.³⁶ For reaction (2), the statistical treatment reproduces the experimental rate constants well assuming a transition state energy only somewhat above that calculated. For reaction (1), the statistical treatment, regardless of input parameters, predicts a too shallow temperature dependence, indicating that the assumed reaction pathway involving that transition state is not dominant.

Instead, the statistical modelling suggests that reaction (1), $\mathrm{Nb}^{\mathrm{+}} + \mathrm{CO}_2,$ at thermal energies is rate-limited by the ISC, while the results for reaction (2), $Ta^+ + CO_2$, are ambiguous and the reaction may be rate-limited by the ISC, a transition state, or a combination of both. Inspection of the calculated reaction pathways for the two reactions show qualitative similarity. In both cases, the ISC is calculated to be close to the transition state. The crossing point for reaction (1) is calculated at ≈ 0.1 eV lower than the transition state and in the product well. The calculated minimum energy path for reaction (1) then does not include any of the calculated transition states, instead the ISC deposits the reaction directly into the product well. This interpretation is consistent with the statistical modelling results; however, both the calculated minimum energy pathway and the statistical modelling are simplifications of a complicated reaction process, and the result cannot be viewed as definitive.

The dynamics of triatomic systems can often be rationalized under the Polanyi rules,²⁹ but these rules are not easily generalized to systems of more than three atoms. Attempting to apply those rules to the current systems by considering the product CO as a single unit suggests an "early" transition state (i.e. close to the reactant well). Under the Polanyi rules, such a potential surface will favour energy disposal into the NbO⁺ or TaO⁺ product vibrations, consistent with the observations here of excess energy being placed into internal modes. The sudden vector projection model (SVP) attempts to generalize the Polanyi rules to larger systems by comparing the vector of the critical mode at the transition state to the vectors of translational, rotational, and vibrational modes in the separated products or reactants.53,58 SVP can only be applied where a process occurs promptly. Here, SVP may not appropriate to apply to the separated reactants, because the reaction proceeds through a longlived intermediate. However, the dissociation of the exit channel complex is expected to be prompt due to the large exothermicity of the reaction and SVP can be applied. Under such circumstances, the energy disposal is largely dictated by the reaction coordinate at the saddle point, as implied by the SVP model. The SVP results for the $[OTaOCO]^+ \rightarrow TaO^+ + CO$ dissociation on the triplet or quintet surfaces are shown in Table 2.

On the triplet surface, the SVP model indicates a preference for internal energy disposal, consistent with the experimental results. The TaO^+ vibration is predicted to be excited, consistent

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 Table 2
 Results of the SVP model for the dissociation of the [TaOCO]⁺

 transition state on the triplet and quintet surfaces. A graphical illustration of modes used in the SVP analysis is given in Fig. S8 (ESI)

	Triplet	Quintet
Translation	0.591	0.150
TaO ⁺ vibration	0.301	0.15
CO vibration	0.071	0.011
TaO ⁺ rotation	0.339	0.682
CO rotation	0.428	0.494

with the Polanyi rules picture above, but primarily the internal energy disposal is expected to be in rotation. Interestingly on the quintet surface, which appears "later" than on the triplet surface, the vibrational excitation is predicted to be very small, consistent with the Polanyi rules, but the deposition into translation is predicted to decrease, inconsistent with the simple picture. The Nb⁺ system has not been treated by SVP, but the similarities between the Ta⁺ and Nb⁺ reaction path dictate that the SVP results would be very similar. In short, the observed dynamics are not inconsistent with the triplet transition state controlling the dynamics.

Conclusions

We presented a multi-method approach to investigate the nature of the bottleneck found for the oxygen atom transfer reactions between Nb⁺ and Ta⁺ with CO₂. Experimental differential cross sections from crossed beam imaging experiments show dominant indirect dynamics for $Nb^+ + CO_2$ as found prior for $Ta^+ + CO_2$. Despite both reactions involving only four atoms and being highly exothermic, we find a high fraction of internal excitation of NbO⁺ and CO as well as the additional collision energy being mostly partitioned into internal excitation. Only at about 2 eV relative collision energy some rebound dynamics set in. To conclude, both reactions show very similar dynamics which are dominated by indirect dynamics due to a bottleneck along the reaction path. To assess the nature of this bottleneck, we performed temperature dependent rate measurements in combination with statistical modelling. Both reactions show a mild negative temperature dependence which could be modelled using by our statistical approach. The model suggests the ISC as rate limiting for $Nb^+ + CO_2$ but we cannot draw any conclusions for $Ta^+ + CO_2$. Comparing the three $M^+ + CO_2$ (M = Ti, Nb, Ta) reactions that have been investigated in this by combination of statistical modelling and temperature dependent rate constants, the derived ISC lifetimes do scale inversely with mass, consistent with the expectation that the ISC occurs more readily with increasing spin-orbit coupling. Our chemical intuition on if a reaction behaves (non-)statistical or statistical seem to be right as often as it is wrong.

Author contributions

M. E. H. and M. M. carried out the crossed beam experiments. M. E. H. and J. M. analysed the crossed beam data. T. W. R. L.

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and S. G. A. carried out the SIFT experiments. T. W. R. L., S. G. A. and B. C. S. analysed the SIFT data. N. S. S. performed the statistical modelling. M. O. performed and analysed the quantum chemical calculations, Y. L. and H. G. performed and analysed the SVP simulations, J. M., S. G. A. and N. S. S. supervised the experiments. J. M., M. O. and N. S. S. prepared the manuscript, J. M. and N. S. S. coordinated the study.

Conflicts of interest

There are no conflicts to declare.

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 Ta^+ and $Nb^+ + CO_2$: Intersystem crossing in ion-molecule reactions

Electronic Supplementary Information

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- Figure S1: Comparison of integrated energy distribution for whole scattering range and pie cut
- Figure S2: Integrated energy distributions from velocity distributions
- Figure S3: Kinetic traces from SIFT experiments for $Ta^+ + CO_2$
- Figure S4: Representative mass traces for $Ta^+ + CO_2$ from SIFT experiments
- Figure S5: Kinetic traces from SIFT experiments for $Nb^+ + CO_2$
- Figure S6: Representative mass traces for $Nb^+ + CO_2$ from SIFT experiments
- Figure S7: Calculated unimolecular rate curves for the product complex MO⁺(CO)
- + Figure S8: Representation of modes for ${\rm TaO^+} + {\rm CO}$ as used in the SVP analysis
- Table S1: $Ta^+ + CO_2$ rate constants
- Table S2: $Nb^+ + CO_2$ rate constants
- Table S3: Energies of stationary points displayed for $Nb^+ + CO_2 \longrightarrow NbO^+ + CO$ reaction coordinate in figure 1
- Table S4: Comparison of relative energies of stationary points for Nb⁺ + CO_2 at DFT (B3LYP), MP2, CCSD level of theory
- Table S5: Bond lengths and angles for exemplary structures along the reaction coordinate for $Nb^+ + CO_2$ and Ta^+CO_2
- Cartesian coordinates and energies for optimized structures for $Nb^+ + CO_2$ at DFT (B3LYP), MP2 and CCSD level of theory.

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Fig. S1 Integrated energy distributions for the whole scattering range ($\theta = 0^{\circ} - 180^{\circ}$, black solid line) and applied pie cut ($\theta = 0^{\circ} - 160^{\circ}$, pink dashed line). The top panel (a,b) shows the product ion velocity distributions with the kinematic cut-offs (green: ground state, orange: first electronically excited state) and the applied pie cut (pink dashed line) superimposed. The middle panel (c,d) shows the internal energy distributions and the bottom panel (e,f) the kinetic energy distributions of NbO⁺. The vertical lines illustrate the respective kinematic cut-offs. The hashed areas show the 1 σ -error from Gaussian error propagation

Table S1 Rate constants for the indicated reactions derived from SIFT data. Uncertainties are dominated by systematic effects, estimates at $\pm 20\%$

	k (x 10^{-10} cm ³ s ⁻¹)	
T(K)	$Ta^+ + CO_2 \longrightarrow TaO^+ + CO$	$TaO^+ + CO_2 \longrightarrow TaO_2^+ + CO_2$
200	4.9	6.7
300	4.5	5.3
400	4.3	4.2
500	4.3	3.6
600	4.0	3.1

Table S2 Rate constants for the indicated reactions derived from SIFT data. Uncertainties are dominated by systematic effects, estimates at $\pm 20\%$

	$k(x10^{-10} \text{ cm}^3 \text{ s}^{-1})$	
T(K)	$Nb^+ + CO_2 \longrightarrow NbO^+ + CO$	$NbO^+ + CO_2 \longrightarrow NbO_2^+ + CO_2$
200	4.5	0.33
300	3.1	0.17
400	2.6	0.13
500	2.4	0.09
600	2.0	0.12

Table S3 Energies of stationary points for preparing figure 1 using the computational approach described in the main text. All values given relative to ${}^5\mathrm{Nb^+}\mathrm{+CO_2}$

	Energy (eV)		
	Quintet	Triplet	Singlet
$Nb^+ + CO_2$	0.00	0.51	1.90
Pre-reaction well (LM1) [NbCO ₂] ⁺	-1.01	-0.66	-0.63
Transition state (TS)	0.84	± 0.00	0.15
Post-reaction well (LM2) [ONbCO] ⁺	0.45	-3.13	-3.05
NbO ⁺ + CO	1.87	-1.99	-1.87



Fig. S2 Comparisons of integrated energy distributions for (a,b) internal, (c,d) NbO⁺ kinetic energy and (e,f) product kinetic energy. The left column directly compares the results for both collision energies. The coloured columns indicate the 1σ -error from Gaussian error propagation and are centred around the respective kinematic cut-offs. The right column shows the mean bin and the bin with maximum intensity of the respective distributions including errors. The error of the relative collision energy stems from the widths of the velocity distributions from the input beams. The error of the respective integrated energy distributions is determined via Gaussian error propagation.



Fig. S3 Representative SIFT data for the Ta⁺ +CO₂ reaction. Data shown is at 300 K, 0.34 Torr, with a reaction time of 2.6 ms. Experimental data are Ta⁺ (black solid circles), TaO⁺ (red solid squares), TaO⁺ (blue solid triangles), TaO⁺(CO₂) (purple open up triangles), TaO⁺₂(CO₂)₂ (darker purple open down triangles), and TaO⁺₂(CO₂)₃ (mauve open side triangles). Curves are fits from kinetic modeling.



Fig. 54 Representative SIFT time-of-flight spectra for the Ta⁺ + CO₂ data shown in figures 4 and S3. Inset shows representative peak shapes.



Fig. S5 Representative SIFT data for the Nb⁺+CO₂ reaction. Data shown is at 300 K, 0.33 Torr, with a reaction time of 2.6 ms. Experimental data are Nb⁺ (black solid circles), NbO⁺ (red solid squares), NbO₂⁺ (blue solid triangles), NbO₂⁺ (CO₂) (purple open up triangles), NbO₂⁺ (CO₂)₂ (darker purple open down triangles), and NbO₂⁺ (CO₂)₃ (mauve open side triangles). Curves are fits from kinetic modelling.



Fig. 56 Representative SIFT time-of-flight spectra for the Nb⁺+CO₂ data shown in figures 4 and S5. Inset shows representative peak shapes.



Fig. S7 Calculated unimolecular rate curves for the product complex (as Figure 5). Top) NbO⁺(CO) and Bottom)TaO⁺(CO) dissociations as a function of internal energy for J = 0, 50, 100, 150, and 200

Table S4 Relative energy (in eV) along the Nb⁺ + CO₂ reaction pathway in three different spin multiplicities, relative to the ${}^{5}Nb^{+}$ + CO₂ limit. Optimization was performed using either DFT (B3LYP), MP2 or CCSD method, CCSD(T) energies are shown, including the zero-point energy as calculated within the respective optimization method. The aug-cc-pVTZ basis set was used for C, O, the ECP28MDF_AVTZ basis set was employed for Nb

		DFT (B3LYP)	MP2	CCSD
Reactants	$^{1}\text{Nb}^{+} + \text{CO}_{2}$	1.90	1.90	1.90
	$^{3}\text{Nb}^{+} + \text{CO}_{2}^{-}$	0.51	0.51	0.51
	${}^{5}\text{Nb}^{+} + \text{CO}_{2}^{-}$	0	0	0
Pre-reaction well (LM1)	¹ [NbOCO] ⁺	-0.53	-0.63	-0.63
	³ [NbOCO] ⁺	-0.63	-0.66	-0.66
	⁵ [NbOCO] ⁺	-0.96	-1.01	-1.01
Transition state (TS)	¹ [NbCO ₂] ⁺	0.17	0.10	0.15
	$^{3}[NbCO_{2}]^{+}$	0.03	0.00	-
	⁵ [NbCO ₂] ⁺	0.86	0.87	0.84
Post-reaction well (LM2)	¹ [ONbCO] ⁺	-3.04	-3.06	-3.05
	³ [NbOCO] ⁺	-3.12	-3.11	-3.13
	⁵ [NbOCO] ⁺	0.48	0.46	0.45
Products	1 NbO ⁺ + CO	-1.87	-1.89	-1.87
	3 NbO ⁺ + CO	-1.98	-1.97	-1.99
	$^{5}NbO^{+}+CO$	1.92	1.87	1.87



Fig. S8 Graphical illustration of modes for the products $TaO^+ + CO$ for the reaction $Ta^+ + CO_2$ together with the imaginary mode at the transition state which represents the dissociation coordinate at the transition state (triplet: orange; quintet: green))

Table S5 Comparison of bond lengths and bond angles f	or $M^+ + CO_2$ ($M = NB$	o, Ta) as optimize	d at the CCSE) level of the	ory along with the
aug-cc-pVTZ basis set was used for C, O, the ECP28MDF	AVTZ basis set for Nb.	and ECP60MDF	AVTZ for Ta.	Transition sta	tes were calculated
at the B3LYP level with the same basis set.					

			Bond ler	ıgth (Å)		Bond an	gles (°)
		$M-O_1$	$O_1 - C$	C-O ₂	M-C	∠(MOC)	∠(OCO)
CO ₂			1.160	1.160			180
pre-reaction well ⁵ [MOCO] ⁺	Nb	2.328	1.184	1.141			180
	Ta	2.209	1.177	1.140			180
Quintet transition state (5TS)	Nb	1.932	1.894	1.126	2.203	70.3	124.0
	Ta	1.922	1.841	1.130	2.138	69.2	124.6
Triplet transition state (³ TS)	Nb	2.117	1.220	1.150	2.568	96.9	163.6
-	Та	2.047	1.227	1.142	2.585	101.3	164.5
CP (quintet \rightarrow triplet)	Nb	1.957	1.313	1.159	2.114	77.8	145.8
	Ta	1.961	1.295	1.158	2.228	83.7	147.1
Post-reaction well ³ [OMCO] ⁺	Nb	1.659		1.118	2.330		
	Та	1.666		1.119	2.201		
³ MO ⁺	Nb	1.651					
	Та	1.654					
СО				1.129			

Cartesian coordinates (in Angstrom) of optimized structures along with their zero-point corrected electronic energies calculated at the respective level (in Hartree)

DFT (B3LYP)		1 [NbCO ₂] ⁺ , LM2	
CO ₂		E = -245.157147	
E = -188.651729		C -0.743551 -1.40389	3 0.000000
O 0.000000 0.00000	0 1.160469	O -1.052322 -2.48487	9 0.000000
C 0.000000 0.00000	0.000000	Nb 0.000000 0.64153	2 0.000000
O 0.000000 0.00000	0 -1.160469	O 1.609985 0.24994	5 0.000000
C0		3 [NbCO ₂] ⁺ , LM2	
F = -113353802		E = -245.159356	
O 0.000000 0.00000	0 0.482499	C -0.778298 -1.46841	7 0.000000
C 0.000000 0.00000	0 -0.643331	O -1.046240 -2.55542	4 0.000000
		Nb 0.000000 0.64731	6 0.000000
¹ [NbCO ₂] ⁺ , LM1		O 1.629964 0.33924	2 0.000000
E = -245.056694			
Nb 0.000000 0.0000	00 1.175071		
O 0.000000 0.0000	00 -1.025194	E = -245.036735	0 000000
C 0.000000 0.0000	00 -2.202791	C -0.808244 -1.30284	s 0.000000
O 0.000000 0.0000	00 -3.344950	0 -1.261/91 -2.41/60	b 0.000000
³ [NbCO ₂] ⁺ IM1		ND 0.000000 0.60654	1 0.000000
E = 245.067084		0 1.912974 0.33122	2 0.000000
E = -243.007084 Nb 0.000000 0.0000	00 1 180411	¹ [NbO] ⁺	
0 0,000000 0,0000	00 -1.035451	E = -131.751190	
C 0.000000 0.0000	00 2 212244	Nb 0.000000 0.000000	0.269203
	00 -2.212344	O 0.000000 0.000000	-1.379667
0 0.00000 0.0000	00 -3.354895	301-01+	
⁵ [NbCO ₂] ⁺ , LM1			
E = -245.089813		E = -131.758230	0.260555
O 2.548513 -0.585	438 0.001061		0.209353
C 1.613785 0.085	345 -0.002380	0 0.000000 0.000000	-1.381408
O 0.867917 1.050	0114 0.000692	⁵ [NbO] ⁺	
Nb -0.902784 -0.103	158 0.000006	E = -131.623554	
		Nb 0.000000 0.000000	0.310122
$[NDCO_2]^2, 13$		O 0.000000 0.000000	-1.589375
E = -245.042789	504 0.000068		
C 0.84004E 1.000		CP (Quintet/Inplet); no ZPE	
C -0.840043 1.099		E = -245.073515, -245.07352	
0 -1.496800 0.036	0312 0.003539	ND -0.82/690 -0.11015	8 -0.000040
0 -2.4//403 -0.580	0254 -0.001429	0 2.444928 -0.52115	5 -0.000610
3 [NbCO ₂] ⁺ , TS		C 1.395265 -0.01646	4 0.001476
E = -245.053496		0 0.750532 1.09806	5 -0.000294
O -2.592156 0.569	017 -0.000443		
C -1.644197 -0.081	556 0.000997		
O -0.874231 -1.027	293 -0.000325		
Nb 0.916983 0.101	355 0.000004		
5[NbCO ₂] ⁺ , TS			
E = -245.018122			
0 1.232377 -0.686	0.000000		
C -0.548077 -1.332	134 0.000000		
0 -0.821319 -2.424	689 0.000000		
Nb -0.000000 0.801	972 0.000000		

MP2			
CO_2			
E = -	188.310147		
0	0.000000	0.000000	1.170226
С	0.000000	0.000000	0.000000
0	0.000000	0.000000	-1.170226
со			
E = -	113,137605		
0	0.000000	0.000000	0.488125
С	0.000000	0.000000	-0.650833
¹ [Nb0	$[0_2]^+, LM1$		
E = -	244.256797		
Nb	0.000000	0.000000	1.224775
0	0.000000	0.000000	-1.109474
С	0.000000	0.000000	-2.292785
0	0.000000	0.000000	-3.447908
³ [Nb0	$[0, 1]^+$, LM1		
E = -	-244.272098		
Nb	0.000000	0.000000	1.209211
0	0.000000	0.000000	-1.078476
С	0.000000	0.000000	-2.266017
0	0.000000	0.000000	-3.419220
5 ГАЛЬС	0.1+ IM1		
	244 200017		
Nb	0.000000	0.000000	1.211917
0	0.000000	0.000000	-1.081809
c	0.000000	0.000000	-2 271934
õ	0.000000	0.000000	- 3.425316
1 rant			
LNPO	$\mathbf{CO}_2 \mathbf{J}^+, \mathbf{TS}$		
E = - Nb	0 833620	0 110002	0 000172
	0.033029	-0.110092	-0.000172
C	-0./01/30	0.002616	-0.001430
	-1.402005	-0.002010	0.000748
3 5 1 4	-2.437114	-0.3491/9	-0.002/31
	$\mathbf{JO}_2 \mathbf{J}^+, \mathbf{TS}$		
E = - Nb	-244.251285	-0 103938	0 000006
0	0.839563	1 054378	0.000081
c	1 552150	0.028503	-0.000335
0	2 565600	0.020305	0.000137
5 5 5 7 1	2.505007	0.545075	0.000137
	$[0_2]^+, TS$		
E = - Nh	-244.206774	0 824531	0 00000
0	1 172872	-0 728175	0.000000
c	-0 556806	-0.720173	0.000000
0	-0.755267	-2.475323	0.000000
lan	0.,0020/	2.1/0020	0.000000
· [Nb($[U_2]^+, LM2$		
E = -	-244.38/368	-1 400755	0.00000
0	-1 053802	-2 505712	0.000000
Nh	-0 000000	0.658062	0.000000
0	1.618824	0.190458	0.000000

³ [NbC	O ₂] ⁺ , LM2		
E = -2	244.386371		
С	-0.775357	-1.502856	0.000000
0	-1.035096	-2.603169	0.000000
Nb	0.000000	0.665322	0.000000
0	1.616613	0.320537	0.000000
⁵ [NbO] ⁺ , LM2		
E = -2	244.226517		
С	-0.874707	-1.413068	0.000000
0	-1.255754	-2.477971	0.000000
Nb	0.000000	0.636120	0.000000
0	1.911785	0.277656	0.000000
¹ [NbO] ⁺		
E = -	131.202282		
Nb	0.000000	0.000000	0.273858
0	0.000000	0.000000	-1.403523
³ [NbO	0] ⁺		
E = -	131.204543		
Nb	0.000000	0.000000	0.269284
0	0.000000	0.000000	-1.380080
⁵ Г N ЬО	1+		
F = -	-		
Nb	0.0000000	0.000000	0.318538
0	0.000000	0.000000	-1.632507

S8

CCSD)		
CO_2			
E = -	-188.298907		
0	0.000000	0.000000	1.159629
С	0.000000	0.000000	0.000000
0	0.000000	0.000000	-1.159629
CO			
E = -	-113.139474		
0	0.000000	0.000000	0.483757
С	0.000000	0.000000	-0.645009
¹ [Nb0	CO ₂] ⁺ , LM1		
E = -	244.271167		
Nb	0.000000	0.000000	1.238169
0	0.000000	0.000000	-1.143892
C	0.000000	0.000000	-2.319508
0	0.000000	0.000000	-3.462094
³ [Nb	$[CO_2]^+$, LM1		
E = -	-244.277241		
Nb	0.000000	0.000000	1.217605
0	0.000000	0.000000	-1.102435
С	0.000000	0.000000	-2.283980
0	0.000000	0.000000	-3.424806
⁵ [Nb	$[CO_2]^+$, LM1		
E = -	-244.296544		
Nb	0.000000	0.000000	1.221051
0	0.000000	0.000000	-1.106832
С	0.000000	0.000000	-2.291185
0	0.000000	0.000000	-3.432664
	$CO_{2}1^{+}$. TS		
E = -	-244.242879		
Nb	0.866351	-0.106594	-0.000068
0	-0.840045	1.099316	-0.000876
С	-1.496800	0.036312	0.003539
0	-2.477403	-0.580253	-0.001429
⁵ [Nb	CO ₂]+, TS		
E = -	-244.222314		
Nb	0.000000	0.822890	0.000000
0	1.205425	-0.712086	0.000000
С	-0.514011	-1.383704	0.000000
0	-0.819917	-2.467447	0.000000
¹ [Nb	$[CO_2]^+$, LM2		
E = -	-244.356034		
С	-0.767515	-1.480727	0.000000
0	-1.040667	-2.566786	0.000000
Nb	0.000000	0.660348	0.000000
0	1.616303	0.293046	0.000000
³ [Nb	$[CO_2]^+$, LM2		
E = -	-244.361131		
С	-0.783497	-1.529999	0.000000
0	-1.043021	-2.617573	0.000000
Nb	-0.000000	0.664660	0.000000
0	1.630644	0.358690	0.000000

⁵ [NbO] ⁺ , LM2			
E = -	244.240456		
С	-0.874623	-1.410369	0.000000
0	-1.254022	-2.465341	0.000000
Nb	-0.000000	0.643502	0.000000
0	1.909989	0.225172	0.000000
¹ [NbO] ⁺			
E = -131.176089			
Nb	0.000000	0.000000	0.269278
0	0.000000	0.000000	-1.380051
³ [NbO] ⁺			
E = -	131.182472		
Nb	0.000000	0.000000	0.269477
0	0.000000	0.000000	-1.381069
⁵ [NbO] ⁺			
E = -	131.051881		
Nb	0.000000	0.000000	0.319471
0	0.000000	0.000000	-1.637289
CP (Quintet/Triplet); not fully converged			
E = -244.266313244.266495			
Nb	-0.660979 -	0.065529	0.003668
0	2.460321	-0.604005	-0.003699
С	1.453202	-0.031124	-0.000576
0	0.874888	1.147521	-0.000013

S9

4.2 QCT simulations compared to the experimental results

In a recent work, Liu et al. reported their findings of further theoretical work done to the oxygen atom transfer (OAT) reaction of the niobium cation and CO_2 (reaction (26)). [131]

$$Nb^+ + CO_2 \longrightarrow NbO^+ + CO$$
 (26)

With this, the open questions of the presented study (chapter 4.1) can be approached:

- Where does the intersystem crossing (ISC) occur?
- What is the bottleneck of the reaction?
- · How is the energy partitioned into the products?

Previously, a potential energy profile already was calculated, suggesting the ISC as the reate determining step but no conclusions could be drawn. To answer these questions Liu et al. conducted further extensive theoretical calculations. They calculated global potential energy surfaces for the quintet, triplet and singlet states and used a trajectory surface hopping method as a semiclassical approach for the treatment of nonadiabatic dynamics as in the present reaction. [131]

For the first question, their results show clearly (Figure 34) that the ISC takes place after the saddle point of the triplet surface and the prereaction complex well of the quintet state. But they also show that the crossing seam of the both surfaces lies before the saddle point of the quintet state. Thus, no saddle point needs to be overcome along the reaction pathway, which is the reason for the high efficiency of the reaction. This reaction pathway is very similar compared to the reaction with the Ta⁺ cation. The lifetimes of the pre-reaction complex are longer in case of niobium, which was assigned to the lower spin-orbit coupling of the lighter homologue. Other than this only absolute energies of the different geometries show small differences. [131, 132]



Figure 34: Potential energy surfaces for the reaction of Nb⁺ + CO₂ \longrightarrow NbO⁺ + CO. The black curve shows the quintet surface, which is the ground state in which the reactions starts, red and blue curves are the triplet and singlet profiles, respectively. (Reprinted with permission from J. Phys. Chem. A 2024, 128, 33, 6943–6953 Copyright 2024 American Chemical Society.)

Together with the results of their semiclassical trajectory simulations, Liu et al. could calculated long lifetimes for the before mentioned prereaction well and short lifetimes for the product complex. Thus, they could confirm that the ISC is the rate limiting step of this reaction, answering the second question. [131]

The third big question was tackled by analyzing the vibrational and rotational distributions of the two products NbO⁺ and CO on basis of the trajectories calculated. The experimental results already showed an indirect character for this reaction, which already could be addressed to the prereaction well. Additionally, increasing the relative collision energy, results in only a little increase in kinetic energy of the products. Therefore, the excess energy must be partitioned into internal degrees of freedom. Theoretical results could reproduce the experimental finding very well. Furthermore, they could conclude that both products are vibrational as well as rotational excited. Especially the vibrational excitation increases when increasing the collision energy of the reactants from 1.3 eV to 2.2 eV. The respective trends are shown in figure Figure 35. Liu et al. could also conclude, that the high internal excitation of the metaloxide cation is analogous to that for the respective reaction with tantalum [131, 132].



Figure 35: Comparison of the calculated energy partitioning among the products NbO⁺ and CO as a function of the collision energy. (Reprinted with permission from J. Phys. Chem. A 2024, 128, 33, 6943–6953 Copyright 2024 American Chemical Society.)

Velocity distributions and DCSs from our experiment were compared to the theoretical results of Liu et al. (Figure 36). Overall a reasonably well agreement can be observed. The experimental and theoretical velocity distributions predominantly show isotropical scattering around the center of mass, indicating the indirect reaction mechanism. Only the DCSs show a discrepancy at the higher collision energy. While experimental results showed higher values for the backwards direction, theory suggests forward direction. The high mass of Nb⁺, additional electronic states or underestimation of the singlet channel by DFT are suggestions to explain this discrepancy. The same goes for the tantalum reaction. [131, 132]



Figure 36: Comparison of the experimental and theoretical results. The top panels show the experimental velocity distributions at 1.3 and 2.2 eV collision energy (a and b), middle two panels the respective theoretical results (c and d) and bottom shows comparisons of the experimental and theoretical DCSs (e and f). (Reprinted with permission from J. Phys. Chem. A 2024, 128, 33, 6943–6953 Copyright 2024 American Chemical Society.)

Overall this is a great example for how cooperation of theory and experiment can benefit from each other. Studies like this can contribute to fundamental research in two ways: Experimental findings that couldn't be explained before can be focused analyzed and new theoretical methods can use the experimental findings as benchmarking system.

5 Conclusion

Gas phase investigations can provide a manifold of information. These can be simple information like the structure and absorption properties of an isolated molecule or more enhanced, like results from reactions. Depending on the experimental setup, such studies can be performed under multi-collision conditions or single-collision conditions. The first one, are typically characterized by higher pressure in the interaction volume and relative long interaction times. In that way thousands of collisions occur, resulting in thermalization of the ions of interest. With that, a distribution around an average specific energy is achieved, reactive states can be trapped or excess energy can be distributed to other particles via the collisions. Single-collision conditions on the other side are usually characterized by higher vacuum and short interaction times. Here, no or far less collisions take place which is not enough to redistribute energy brought to into the system. In that way, state specific studies are possible, as well as the energy in one specific system is known accurately. When measuring ion-molecule reactions of model systems for catalysis, one can take advantage of these properties. While in multi-collision conditions, a thermal distribution of the ions and molecules is present usually kinetics can be measured. This typically provides information like product distribution or rate constants of the whole reaction or different steps of it. Under single-collision conditions instead, usually dynamics of a reaction are measured. This includes studying the elemental steps of one reaction and measuring cross sections. In the present work, these were the two main topics investigated and discussed.

The first one deals with kinetic measurements inside the trap of a commercial Bruker amaZon ETD mass spectrometer. As a first step, complexes of the type $[M(dgpy)_2]^{n+}$, with M = V - Ni were characterized in gas phase by collision induced dissociation, electron transfer dissociation and ultraviolet photodissociation experiments. The ETD experiments revealed further ionic species to investigate in gas phase. In this way more than just the given oxidation state of the solid, which was used for solution preparation, are accessible. Results from the CID experiments show similar fragmentation pathways and fragments for the most species, also among the different central transition metal ions. Results from UVPD measurements provided gas phase UV/Vis spectra, that show reasonably good agreement with absorption spectra from solution. The next step was the setup of an extension of the mass spectrometer to insert reactive gases into the Paul trap. This was necessary to investigate ion-molecule reactions in the gas phase. This is, to exclude the most external influences and work with well defined conditions. There is a huge interest for ion-molecule reactions in gas phase, as already

5 Conclusion

presented in the introduction, because in that way model systems for catalysts and their reactions can be investigated in a very controlled manner. The present experimental results show, that the setup was successful and first reactions already could be measured. With the before mentioned complexes the oxidation of triethylamine was investigated. It was only shown to take place for manganese(IV), manganese(III) and iron(III) in their respective ground state. However, these experiments were of proof-of-principal character, preparing the way for further kinetic experiments.

A few exceptions among the reduced species were observed, where CID fragmentation patterns hint towards reduced ligand species. To tackle this open question further, infrared multiphoton dissociation measurements at the free electron laser FELIX were attempted and need to be supplemented with input from theoretical work. The ion-molecule experiments that were conducted, cannot be quantified yet in terms of calculating thermal rate constants. This is because the density of the neutral molecules is not determined, yet. But first calibration measurements are already conducted, also shown here. First experiments with laser excitation of the ions before the reaction takes place were performed and showed positive results with the cobalt(III) species **Co[III,0]3+**. Overall this shows that the modifications made, help to get a better understanding of structure and reactivity and will eventually open the field for investigations of photocatalysts.

The second topic of this work is about the dynamics of the oxygen atom transfer reaction of the niobium cation with CO₂. With a crossed beam 3D velocity map imaging spectrometer the respective reaction was measured. Angle and energy differential cross sections were obtained. In cooperation with theoretical work, this reaction as well as the same reaction with the tantalum cation could be investigated and explained in more detail than ever before. The reaction pathway was examined in a collaborative work of experiment and theory. Since the origin of the high efficiency of this reaction was a two-state reactivity, the position of the ISC was determined in this work. It could be stated that it is in fact the rate determining step along the reaction pathway. In addition product energy partitioning could be disentangled. High rotational and vibrational excitation for the metaloxide ion were found for the reaction of niobium similar to tantalum. The present results, are providing important insights on the OAT reaction for the cations of niobium and tantalum and in general for this type of reaction overall. For the theory this collaborative work was a way to benchmark their methods.

For both experiments future modifications or advancements are already planned out. In this way, as mentioned before the gas mixing unit from the amaZon ETD will be moved to the amaZon Speed. Then there will be calibration measurements performed

5 Conclusion

to determine the density of the neutral molecules inside the trap, as already shown for the amaZon ETD. When these demanding measurements are finished, thermal rate constants of model systems and their reactions will be accessible. With the option of optical access, reactions in the electronically excited state should be studied. Combined with the possibilities in gas phase and especially in the ion trap to create new species that might not be accessible in condensed phase, will make it to a rather strong tool in catalysis research.

The VMI experiment will get two specific modifications. One is a quadrupole ion bender unit and the other a linear multipole iontrap. Both will be in the pathway of the ion beam in front of the VMI chamber. With this, probably selectivity of the ions will increase, as well as the precision in ion energy. The trap will also enable us to create and investigate reactive intermediate species like MCH₂⁺ or MO⁺. In that way, increasing the size of the reactants will become possible. Additionally a laser setup for further characterization will be added, to investigate specific excited states of ions or molecules and even further increase the precision of the experiment.

The two projects show, that with different experimental setups a variety on systems and reactions can be measured, both with their own specific advantages. On one side there is the ESI source, which is able to provide for many different ions that are present in solution. With a mass range of m/z depending only on the analyzer and detector. In the present case, a window of 50 - 3000 m/z, a lot of different molecules can be investigated precisely. The Paul trap additionally provides the opportunity to trap ions and do experiments in several MS/MS steps. As it could be shown, the MS provides a lot of information, especially with the current expansion. In that way kinetic measurements like rate constants under multi-collision conditions and other qualitative properties are readily accessible. On the other side, the VMI setup with its laser vaporization source can generate pure metal cations or clusters which can be investigated with regard to catalysis on metal surfaces or just as model for a reactive center of a catalyst. A different perspective on reactions, namely the dynamics of model systems, can be obtained by the VMI experiment. Giving angle and energy DCSs, which is a level of detail that not many experiments can achieve, these experiments are well suited for benchmarking theory.

6 Literature

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7.1 Mass spectra



Figure 37: Overview mass spectrum of the solution of $[V(dgpy)_2](OTf)_3$ (a) and the resulting spectra of the ETD process with the species V[III,0]3+ (b) and V[III,1]2+ (c), respectively. The arrows show the reduction steps to the species of interest.



Figure 38: Comparison of the mass spectra of the isolated species obtained from the solution of $[V(dgpy)_2](OTf)_3$ compared to the respective simulated spectrum as labeled.



Figure 39: Overview mass spectrum of the solution of $[Cr(dgpy)_2](PF_6)_3$ (a) and the resulting spectra of the ETD process with the species **Cr[III,0]3+** (b) and **Cr[III,1]2+** (c), respectively. The arrows show the reduction steps to the species of interest, other signals are fragments (*1 = $[Cr(dgpy)]F^+$ and *2 = $[Cr(dgpy)_2]F^+$).



Figure 40: Comparison of the mass spectra of the isolated species obtained from the solution of $[Cr(dgpy)_2](PF_6)_3$ compared to the respective simulated spectrum as labeled.



Figure 41: Overview mass spectra of the solutions of $[Fe(dgpy)_2](PF_6)_3$ (a) and $[Fe(dgpy)_2](PF_6)_2$ (b) and the resulting spectra of the ETD process with the species **Fe[III,0]3+** (c), **Fe[II,0]2+** (d) and **Fe[III,1]2+** (e) respectively. The arrows show the reduction steps to the species of interest.



Figure 42: Comparison of the mass spectra of the isolated species obtained from the solutions of $[Fe(dgpy)_2](PF_6)_3$ and $[Fe(dgpy)_2](PF_6)_2$ compared to the respective simulated spectrum as labeled.



Figure 43: Overview mass spectrum of the solution of $[Co(dgpy)_2](BF_4)_3$ (a) and the resulting spectra of the ETD process with the species **Co[III,0]3+** (b) and **Co[III,1]2+** (c), respectively. The arrows show the reduction steps to the species of interest.



Figure 44: Comparison of the mass spectra of the isolated species obtained from the solution of $[Co(dgpy)_2](BF_4)_3$ compared to the respective simulated spectrum as labeled. The signal at 765 m/z could not be isolated.



Figure 45: Overview mass spectrum of the solution of $[Ni(dgpy)_2](BF_4)_2$ (a) and the resulting spectrum of the ETD process with the species **Ni[II,0]2+** (b). The arrow shows the reduction step to the species of interest.



Figure 46: Comparison of the mass spectra of the isolated species obtained from the solution of $[Ni(dgpy)_2](BF_4)_2$ compared to the respective simulated spectrum as labeled.

7.2 CID curves



Figure 47: Comparison of the CID curves against the respective E_{COMz} values of the five investigated vanadium species as labeled.



Figure 48: Comparison of the CID curves against the respective E_{COMz} values of the five investigated chromium species as labeled.



Figure 49: Comparison of the CID curves against the respective E_{COMz} values of the five investigated iron species as labeled.



Figure 50: Comparison of the CID curves against the respective E_{COMz} values of the five investigated cobalt species as labeled.



Figure 51: Comparison of the CID curves against the respective E_{COMz} values of the three investigated nickel species as labeled.



Figure 52: Comparison of the CID curves of all precursor ions against the respective E_{COMz} values. Same colors indicate comparable species in the means of oxidation state, counter ion number and charge state.

7.3 UVPD measurements



Figure 53: UVPD spectra of all species of $[V(dgpy)_2](OTf)_3$. The black and the red traces are only a result of overall low photofragmentation and therefore are not discussed in the respective chapter.



Figure 54: UVPD spectra of all species of $[Fe(dgpy)_2](PF_6)_2$ or $[Fe(dgpy)_2](PF_6)_3$. The red spectrum shows no photofragmentation and therefore it is not discussed in the respective chapter.



Figure 55: UVPD spectra of all species of $[Co(dgpy)_2](BF_4)_3$. The black and the red traces are only a result of overall low photofragmentation and therefore are not discussed in the respective chapter.



Figure 56: UVPD spectra of all species of $[Ni(dgpy)_2](BF_4)_2$. The black spectrum shows almost no photofragmentation and therefore it is not discussed in the respective chapter. But as discussed, the blue spectrum is not very meaningful because of auto fragmentation.



Figure 57: Power dependent measurements of $[V(dgpy)_2](OTf)_3$ at 265 and 320 nm. The allometric fit results are next to the spectra. In the cases where the fit did not converge, it was omitted.



Figure 58: Power dependent measurements of $[Fe(dgpy)_2](PF_6)_2$ or $[Fe(dgpy)_2](PF_6)_3$ at 265 and 320 nm. The allometric fit results are next to the spectra. In the cases where the fit did not converge, it was omitted.



Figure 59: Power dependent measurements of $[Co(dgpy)_2](BF_4)_3$ at 265 and 320 nm. The allometric fit results are next to the spectra. In the cases where the fit did not converge, it was omitted.



Figure 60: Power dependent measurements of $[Ni(dgpy)_2](BF_4)_2$ at 265 and 320 nm. The allometric fit results are next to the spectra. In the cases where the fit did not converge, it was omitted.



Figure 61: Fragment specific UVPD spectra for the species of $[V(dgpy)_2](OTf)_3$, which showed relevant photo induced fragmentation. The error bars are omitted for clarity.



Figure 62: Fragment specific UVPD spectra for the species of $[Fe(dgpy)_2](PF_6)_2$ or $[Fe(dgpy)_2](PF_6)_3$, which showed relevant photo induced fragmentation. The error bars are omitted for clarity.



Figure 63: Fragment specific UVPD spectra for the species of $[Co(dgpy)_2](BF_4)_3$, which showed relevant photo induced fragmentation. The error bars are omitted for clarity.



Figure 64: Fragment specific UVPD spectra for the species of $[Ni(dgpy)_2](BF_4)_2$, which showed relevant photo induced fragmentation. The error bars are omitted for clarity.

7.4 IRMPD measurements



Figure 65: First results of the IRMPD measurements at FELIX for the species **Fe[III,0]3+** (a) and **Fe[II,0]2+** (b) at given attenuation.



Figure 66: First results of the IRMPD measurements at FELIX for the species Co[III,0]3+ (a), Co[III,1]2+ (b), Co[III,2]1+ (c), Co[III,0]2+ (d) and Co[II,1]1+ (e) at given attenuation.

List of publications

Part of the present thesis

- Maximilian E. Huber, Adela Ceman, Philipp Weber, Lisa Berg, Nathan R. East, Christoph Riehn, Katja Heinze, and Jennifer Meyer
 Gas-Phase Characterization of Redox-Active Manganese Complexes J. Am. Soc. Mass Spectrom. (2024), 35, 11, 2642-2649. https://doi.org/10.1021/jasms.4c00113
- Maximilian E. Huber, Tucker W. R. Lewis, Marcel Meta, Shaun G. Ard, Yang Liu, Brendan C. Sweeny, Hua Guo, Milan Ončák, Nicholas S. Shuman, and Jennifer Meyer *Ta⁺ and Nb⁺ + CO₂: intersystem crossing in ion–molecule reactions* Phys. Chem. Chem. Phys. (2024), 26, 8670-8680. https://doi.org/10.1039/D3CP05549C

Publications with co-authorship

- Julian Uebel, Yvo Stiemcke, Maximilian E. Huber, Carl Rheinländer, Stefan Thielen, Oliver Koch, Norbert Wehn, and Jörg Seewig Erprobung einer miniaturisierten Infrarotspektroskopie zur Messung von Alterungseffekten in Öl Tech. Mess. (2024), 91, 10, 515-523. https://doi.org/10.1515/teme-2024-0058
- Marcel Meta, Maximilian E. Huber, Maurice Birk, Martin Wedele, Milan Ončák, and Jennifer Meyer
 Dynamics of carbene formation in the reaction of methane with the tantalum cation in the gas phase
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- Daniela V. Fries, Matthias P. Klein, Annika Straßner, Maximilian E. Huber, and Gereon Niedner-Schatteburg *Cryo-IR spectroscopy and cryo-kinetics of cluster N₂ adsorbate complexes of tantalum cluster cations Ta₅₋₈⁺* J. Chem. Phys. (2023), 159, 164306. https://doi.org/10.1063/5.0157218
- Daniela V. Fries, Matthias P. Klein, Annika Straßner, Maximilian E. Huber, Maximilian Luczak, Christopher Wiehn, and Gereon Niedner-Schatteburg Cryo IR spectroscopy and cryo kinetics of dinitrogen activation and cleavage by small tantalum cluster cations
 J. Chem. Phys. (2023), 159, 164303. https://doi.org/10.1063/5.0157217
- Marcel Meta, Maximilian E. Huber, Tim Michaelsen, Atilay Ayasli, Milan Ončák, Roland Wester, and Jennifer Meyer Dynamics of the Oxygen Atom Transfer Reaction between Carbon Dioxide and the Tantalum Cation
 J. Phys. Chem. Lett. (2023), 14, 24, 5524-5530. https://doi.org/10.1021/acs.jpclett.3c01078
- Raphael I. Petrikat, Sophie T. Steiger, Elham Barani, Pit J. Boden, Maximilian
 E. Huber, Mark R. Ringenberg, Gereon Niedner-Schatteburg, Karin Fink, and Sabine Becker

Cooperativity-Driven Reactivity of a Dinuclear Copper Dimethylglyoxime Complex

Chem. Eur. J. (2023), 29, e202203438. https://doi.org/10.1002/chem.202203438

 Masahiro Shibuta, Maximilian E. Huber, Toshiaki Kamoshida, Kazuya Terasaka, Miho Hatanaka, Gereon Niedner-Schatteburg, and Atsushi Nakajima Size-Dependent Oxidative Stability of Silicon Nanoclusters Mixed with a Tantalum Atom
 J. Phys. Chem. C (2022), 126, 9, 4423-4432.

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 Matthias P. Klein, Amelie A. Erhard, Maximilian E. Huber, Annika Straßner, Daniela V. Fries, Sebastian Dillinger, Jennifer Mohrbach, and Gereon Niedner-Schatteburg Cryo infrared spectroscopy of N_2 adsorption onto bimetallic rhodium-iron clusters in isolation

J. Chem. Phys. (2022), 156, 014302. https://doi.org/10.1063/5.0075289

 Annika Straßner, Matthias P. Klein, Daniela V. Fries, Christopher Wiehn, Maximilian E. Huber, Jennifer Mohrbach, Sebastian Dillinger, Dirk Spelsberg, Peter B. Armentrout, and Gereon Niedner-Schatteburg *Kinetics of stepwise nitrogen adsorption by size-selected iron cluster cations: Evidence for size-dependent nitrogen phobia* J. Chem. Phys. (2021), 155, 244306. https://doi.org/10.1063/5.0064965

Yanik Becker, Maximilian E. Huber, Sabine Becker, Yu Sun, Gereon Niedner-Schatteburg, and Werner R Thiel A gas-phase study on the cyclometallation of a series of Cp*Ir(III) complexes bearing bidentate pyrimidine ligands
J. Organomet. Chem. (2021), 954-955, 122063. https://doi.org/10.1016/j.jorganchem.2021.122063

List of conference contributions

Oral presentations

- Gas phase investigations on redox-active complexes of the type [M(dgpy)₂]ⁿ⁺
 72nd Conference on Mass Spectrometry and Allied Topics (ASMS2024)
 Anaheim, CA, USA 02.-06.06.2024
- Gas phase investigations on the redox-active complex [Mn(dgpy)₂]ⁿ⁺
 123. Bunsentagung
 Aachen, Germany 25.-27.03.2024
- Gas phase investigations on the redox-active complex [Mn(dgpy)₂](PF₆)₄
 12. Promovierendenseminar Fachbereich Chemie Kaiserslautern, Germany 16.10.2023

Poster presentations

- Gas phase investigations on the redox-active complex [Mn(dgpy)₂]ⁿ⁺
 24th Symposium on Atomic, Cluster and Surface Physics (SASP2024)
 Andalo, Italy 28.01.-02.02.2024
- Reactive scattering of the oxygen atom transfer reaction between carbon dioxide and group V cations
 DPG Spring Meeting (SAMOP) Hannover, Germany 05.-10.03.2023
- Gas phase investigations on redox-active complexes of the type [M(dgpy)₂]ⁿ⁺ (M = 3d transition metal; n = 1-4)
 122. Bunsentagung Berlin, Germany 05.-07.06.2023

List of student projects co-supervised by myself

- Adela Ceman, master's thesis (2024)
 Reactivity of Isolated Transition Metal Complexes via Irradiation in a 3D Paul Trap²
- Daniel Langhauser, bachelor's thesis (2023) Untersuchung des Komplexes [Cr(dgpy)₂]³⁺ mittels Elektrospray-Ionisations- Massenspektrometrie
- Adela Ceman, student research internship (2023) Untersuchungen des redoxaktiven Mangankomplexes [Mn(dgpy)₂]^{3+/4+} mit unterschiedlicher Anzahl an Gegenionen
- Noel Grimm, student research internship (2023) Dichtekalibrierung einer Quadrupol Ionen-Falle
- Lisa Berg, bachelor's thesis (2023)
 Massenspektrometrische Untersuchungen des redoxaktiven Mangankomplexes [Mn(dgpy)₂]⁴⁺
- Sarah Schröck, master's thesis (2022)
 Spektrometrische Untersuchungen an derivatisierten Azobenzolen³
- Janek Jost, **student research internship** (2022) *Bis(imino)pyridine Iron complexes for ethene polymerization in the gasphase*
- Marvin Theisen, **master's thesis** (2022) Erzeugung und Untersuchung reaktiver Zwischenstufen an einem Paulfallen- Massenspektrometer

²in cooperation with Philipp Weber, working group Christoph Riehn (RPTU Kaiserslautern-Landau) ³in cooperation with Annika Pick, working group Sabine Becker (TU Kaiserslautern)

Curriculum Vitae

Akademische Laufbahn

- 02/2025	RPTU Kaiserslautern-Landau, Germany
	Dr. rer. nat., Chemistry, JunProf. Dr. J. Meyer
	"Dynamics and kinetics of ion-molecule gas phase reactions:
	Investigations of model systems relevant for catalysis"
- 02/2021	TU Kaiserslautern, Germany
	Started doctoral thesis at the group of Prof. Dr. Dr. Gereon Niedner-
	Schatteburg, but switched to JunProf. Dr. J. Meyer
- 12/2019	TU Kaiserslautern, Germany
	Master of Science, Chemistry
	"Charakterisierung von Münzmetallkomplexen mit Phosphinoliganden
	mittels stoßinduzierter Dissoziation und Infrarot-Multiphotonen-
	Dissoziation"
- 09/2017	TU Kaiserslautern, Germany
	Deckelan of Ociana of Okamintary

- Bachelor of Science, Chemistry "Synthese und Charakterisierung von Eisen(II)-Komplexen mit verschiedenen Pyridincarboxylat- und Pyrazincarboxylatliganden"
- 03/2015 Immanuel-Kant-Gymnasium Pirmasens, Germany Abitur

Weiterbildungen

- 11/2024 Online-Seminar: Dein Job in der chemischen Industrie
- 03/2024 Seminar: Moderation von Meetings und Projektbesprechungen
- 08/2023 Seminar: Der Laserschutzbeauftragte (LSB) nach OStrV § 5
- 03/2022 Online-Seminar: Scientific Writing
- 06/2021 Online-Seminar: Minecraft Srum-Workshop
- 12/2020 Online-Seminar: Project managment for scientists
- 12/2020 Online-Seminar: Führen auf Distanz

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Eidesstattliche Erklärung

Hiermit bestätige ich, Maximilian Emil Huber, dass die vorliegende Dissertation

Dynamics and kinetics of ion-molecule gas phase reactions: Investigations of model systems relevant for catalysis

gemäß der Promotionsordnung des Fachbereichs Chemie der Technischen Universität Kaiserslautern (ab 01.01.2023 Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau) selbständig und unter Verwendung keiner anderen, als den angegebenen Quellen und Hilfsmittel, verfasst wurde. Koorperationsprojekte mit anderen Arbeitsgruppen, sowie die beteiligten Mitarbeiter sind an den entsprechenden Stellen abgegrenzt.

Die vorliegende Arbeit wurde bei keiner anderen Hochschule als der Technischen Universität Kaiserslautern (ab 01.01.2023 Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau) in ähnlicher oder gleicher Form eingereicht.

Kaiserslautern,

Maximilian Emil Huber