

Cationic Noncovalent Interactions: Energetics and Periodic Trends

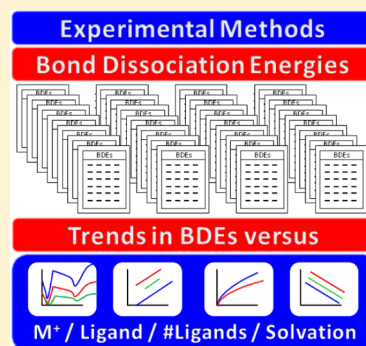
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ABSTRACT: In this review, noncovalent interactions of ions with neutral molecules are discussed. After defining the scope of the article, which excludes anionic and most protonated systems, methods associated with measuring thermodynamic information for such systems are briefly recounted. An extensive set of tables detailing available thermodynamic information for the noncovalent interactions of metal cations with a host of ligands is provided. Ligands include small molecules (H_2 , NH_3 , CO , CS , H_2O , CH_3CN , and others), organic ligands (O- and N-donors, crown ethers and related molecules, MALDI matrix molecules), π -ligands (alkenes, alkynes, benzene, and substituted benzenes), miscellaneous inorganic ligands, and biological systems (amino acids, peptides, sugars, nucleobases, nucleosides, and nucleotides). Hydration of metalated biological systems is also included along with selected proton-based systems: 18-crown-6 polyether with protonated peptides and base-pairing energies of nucleobases. In all cases, the literature thermochemistry is evaluated and, in many cases, reanchored or adjusted to 0 K bond dissociation energies. Trends in these values are discussed and related to a variety of simple molecular concepts.



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I. INTRODUCTION

In their 2000 review of noncovalent interactions,¹ Müller-Dethlefs and Hobza defined these as follows: “Noncovalent interactions originate from interaction between permanent multipoles, between a permanent multipole and an induced multipole, and finally, between an instantaneous time variable multipole and an induced multipole.” Such a definition makes it clear that the introduction of an ionic component will enhance the strength of such interactions considerably as the interactions of a charge with permanent and induced multipoles are longer range as well as intrinsically stronger. Interestingly, in their book on the same subject,² the only ionic system discussed is hydration of the proton, $\text{H}^+(\text{H}_2\text{O})_x$ (which arguably is actually covalent).

Alternatively, one can artificially break down various noncovalent interactions into several categories, and then consider how shifting to ionic systems might change them. Such categories include (a) electrostatic, (b) van der Waals (dispersion) forces, (c) hydrophobic, (d) π -effects, and (e) charge transfer (salt bridges). Electrostatic forces in neutral molecules are the interactions between permanent multipoles and other permanent multipoles or induced multipoles, and as above, such forces are greatly enhanced by replacing the permanent multipole by a charged particle. van der Waals forces are the induced multipole–induced multipole component in the definition above and are strictly replaced by electrostatic interactions once an ion is introduced. Hydrophobic effects occur because the polar parts of a molecule prefer to interact strongly with the solvent in aqueous media, such that the nonpolar parts will tend to associate. As such, hydrophobic effects are intrinsically condensed phase phenomena that can potentially be reproduced by microscopic solvation in the gas phase. In general, the hydrophobic effect in ionic noncovalent interactions is an oxymoron as the ion is intrinsically the polar part of the molecule and will be hydrated efficiently. π -Effects will be enhanced by the presence of an ion as charged species will readily associate with the multipole associated with aromatic systems. Finally, charge transfer is the means by which neutral molecules enhance the mutual interaction by creating a salt bridge. In some cases, the presence of an ion can help induce such charge transfer, and in other cases, the ion can disrupt such interactions by preferentially interacting with one of the charge transfer sites.

One consequence of the enhanced strength of noncovalent interactions when an ion is involved is that the strength of the interaction no longer provides a clear delineation with respect to covalent versus noncovalent. For instance, the strongest bonds included in the tables below (Cu^+ or Zn^+ interacting with phenanthroline) have a bond strength of 395 kJ/mol.^{3,4} This is an appreciable fraction of the covalent H_2 bond energy (432 kJ/mol) and comparable to the C–C single bond energy in ethane (368 kJ/mol). Thus, the characterization of an ionic

noncovalent bond is necessarily determined using other than thermochemical criteria.

I.A. Scope

One thing that became apparent in researching this review is the enormous amount of literature concerning ionic noncovalent interactions. Without restricting the topic in some fashion, this article could easily have filled the entire issue (and required the devoted time of both authors for more than a year). In some measure, this is revealed by the many reviews that precede this one, to which the interested reader is referred for more detailed examinations of parts of the present opus. These include a general review in 1986 by Keesee and Castleman,⁵ examination of cation– π interactions by Dougherty,^{6,7} a review of protonated systems by Meot-Ner,⁸ a review of our own work (largely metals),^{9–11} reviews of individual metal cations interacting with ligands— Li^+ ,^{12,13} Cs^+ ,¹⁴ Al^+ ,¹⁵ and comprehensive¹⁶—and a review concentrating on supramolecular chemistry.¹⁷

The present work concentrates on ionic systems for which experimental gas-phase thermochemistry exists, and is presented in the form of bond dissociation energies (BDEs) (or enthalpies), rather than heats of formation. It does not include species in solution, on surfaces, or on metal clusters, although microsolvation of some biological systems is considered. It does not include theoretical treatments or spectroscopic studies except as they relate to the thermochemistry presented. The thermochemistry does not include values for ionization energies, electron affinities, proton affinities, or proton basicities, generally because such information pertains to covalent interactions. In addition, thermodynamic information on protonated systems is nicely summarized elsewhere.^{8,18} Anionic systems are not included, primarily to limit the scope of this treatise. Anionic systems can be found in the early Keesee and Castleman review,⁵ and anion– π interactions with haloarenes have been reviewed recently.¹⁹ In addition, direct comparisons of the ligand affinities of two different metal cations to one another are not included in this review, largely because such comparisons have been presented in many other reviews and in the original literature.

II. INSTRUMENTAL APPROACHES

A key advantage to studying ionic noncovalent interactions is the ready availability of a variety of mass spectrometric tools appropriate for their experimental study. In this section, we again focus on methods that enable thermodynamic information to be extracted. Although multiple spectroscopic methods have been utilized to provide structural characterization of noncovalent complexes, these methods are not included here. For a more comprehensive assessment of various methods discussed here, the interested reader is referred to an excellent review by Ervin.²⁰

In the tabulated results, we have tried to be comprehensive in indicating the type of experiment utilized in each study, as this has implications for the accuracy and precision of the result. To this end, we utilize a one-letter code for the methods used most commonly: A = radiative association kinetics, B = blackbody infrared radiative dissociation, C = threshold collision-induced dissociation, D = kinetic energy release distribution, E = equilibrium measurement at a single temperature, H = high-pressure temperature-dependent equilibrium, I = photoionization threshold, K = kinetic method, M = mobility, P =

photodissociation, R = ion–molecule reaction bracketing, S = scattering, and T = threshold of endothermic reaction.

II.A. Radiative Association Kinetics (A)

Whereas many of the experiments discussed in Section II determine thermochemistry by inducing dissociation, radiative association examines the formation of a bond of interest and stabilization of the resulting complex by emission of infrared photons.²¹ This generally slow process can only be measured accurately at low pressure such that collisional effects are avoided; hence the use of an ion cyclotron resonance mass spectrometer (ICR-MS) is typical. The rates of the association process are then interpreted using standard kinetic theories (necessarily including the emission rate of the IR photons), in which the lifetime of the association complex is strongly coupled to the energy of the bond being formed. Ideally such experiments are carried out at different temperatures, but this is not always realized. The process is limited to systems where the association is not too fast or too slow, such that binding energies in the range of 50–150 kJ/mol are accessible.

II.B. Blackbody Infrared Radiative Dissociation (BIRD, B)

Blackbody infrared radiative dissociation (BIRD) is an equilibrium method in which ions are heated to the ambient temperature by absorption of the background infrared radiation.^{22–24} Such experiments require the use of an ion trap and a collision-free environment, such that an ICR-MS is most commonly used. (Because no vacuum is entirely collision-free, it is also important to carefully thermalize the kinetic energy of the ions to avoid collision-induced dissociation artifacts.) By systematically varying the temperature of the trap, the rate of dissociation of the ion changes and can be quantitatively modeled, typically using either a simple Arrhenius interpretation or a more complicated Master equation approach. This method is limited by the temperature range available to the apparatus, with 200–500 K being possible and above 300 K being typical. The BIRD approach has allowed BDEs ranging from 50 to 250 kJ/mol to be measured.

II.C. Threshold Collision-Induced Dissociation (TCID, C)

Threshold collision-induced dissociation (TCID) experiments^{25,26} take advantage of the fact that electric fields can easily accelerate charged particles to hyperthermal kinetic energies. This kinetic energy can be transferred into internal energy by collision with an unreactive species (often a rare gas, but other gases and surfaces can also be used). If the energy transferred exceeds a bond energy of the ionic species (the threshold), dissociation ensues with the extent of dissociation depending on the amount of energy transferred, the number of collisions that occur, the complexity of the ion, and the time scale over which the fragmentation is detected. In CID experiments, the distribution of energy transferred from kinetic to internal energy is broad, a consequence that the collisions can occur over a range of impact parameters (unless a surface is used, but then the distribution of energy transferred to the surface becomes an issue). Such experiments can be performed in any tandem mass spectrometer (e.g., a triple quadrupole, QQQ), although a guided ion beam tandem mass spectrometer (GIBMS)^{27,28} provides specific advantages for performing such quantitative studies. In a GIBMS, the radio frequency octopole ion guide in the collision region allows very low and well-controlled collision energies, allows excellent collection of product ions, and avoids collisions of unknown energy outside of the reaction region.

The kinetic energy dependent cross sections for dissociation can be analyzed to determine the threshold for dissociation, which corresponds directly to the bond energy of interest as long as there is no barrier in excess of the product asymptote (a “loose” transition state). This is commonly true for ion–molecule interactions.²⁹ For accurate thermodynamic information to be derived, this analysis must include consideration of the distribution of internal energy of the reactant ions before collision (which depends critically on the source and source conditions),³⁰ the distribution of kinetic energies of both reagents,²⁷ the efficiency of the energy transfer during collision,³¹ the number of collisions (ideally cross sections are extrapolated to single collision conditions before analysis),³² the kinetics of dissociation (including entropic and lifetime effects, which requires some knowledge of the molecular parameters of the ion complex and its dissociation transition state),³³ competition between reaction channels,³⁴ and sequential dissociations.³⁵ Methods for modeling all of these effects are detailed in the literature and have been demonstrated to provide accurate thermodynamic information.^{36–43} Because the kinetic energy range available to such instruments can cover 4 orders of magnitude, there is essentially no limitation to the strength of bonds that can be measured using this technique.

II.D. Kinetic Energy Release Distribution (KERD, D)

In a kinetic energy release distribution experiment,⁴⁴ a reverse geometry double focusing mass spectrometer (magnetic field sector followed by an electric field sector) is used to mass select an ion complex generated in the source and then measure the kinetic energy distribution of the ionic fragments formed by metastable decomposition in the field free region between the sectors. If the internal energy of the ion complex is well-defined, statistical kinetic theory can be used to predict how the available energy is distributed between kinetic and internal degrees of freedom of the products, where one key unknown is the bond energy for the dissociation reaction. By matching the experimental KERD, the value of the BDE can be determined. Such statistical theories are only applicable to reactions for which there is no barrier in excess of the product asymptote (“loose” transition state), which is often the case for ion–molecule interactions, and requires some knowledge of the molecular parameters of the dissociating complex and its products.

II.E. Equilibrium Measurement at a Single Temperature (E)

In section II.F, temperature dependent equilibria coupled with the van't Hoff equation are discussed. However, not all instruments are designed to vary temperature easily. In such cases, reaction equilibrium can still be achieved at the ambient temperature (routinely assumed to be room temperature, but can be elevated by the methods used to generate the ions). In such cases, free energies of reaction can be determined from the equilibrium constant, $\Delta G = -RT \ln K$. In the absence of temperature dependent data, these free energies can be adjusted to enthalpies using a calculated or estimated entropy of reaction, $\Delta H = \Delta G + T\Delta S$. In several of the tables below, we (or others previously) have performed such adjustments to free energy information available in the literature. Such experiments are commonly conducted in ion traps, often an ion cyclotron resonance mass spectrometer (ICR-MS), which generally restricts the reactions to ligand exchange processes, $ML_A^+ + L_B \leftrightarrow ML_B^+ + L_A$, such that only relative thermodynamic information is obtained.

II.F. High-Pressure Temperature-Dependent Equilibrium (H)

Perhaps the most rigorous means of determining thermochemistry is to measure the equilibrium concentration of reactants and products as a function of temperature.⁴⁵ Using the van't Hoff equation, $\ln K = -\Delta G/RT = -\Delta H/RT + \Delta S/R$, a plot of $\ln K$ versus $1/T$ yields the enthalpy (ΔH) and entropy (ΔS) of reaction over the temperature range utilized. Typical devices used are high-pressure mass spectrometers (HPMS) where a bath gas is utilized to ensure rapid equilibration between reactants and products, e.g., $ML_{x-1}^+ + L \leftrightarrow ML_x^+$. Pulsed (PHPMS) variants allow the kinetics leading to equilibrium to be monitored. These experiments are potentially subject to perturbations associated with sampling the equilibrium zone, subsequent ion losses and dissociation, and uncertainties in the absolute temperature. If the temperature range used to make the measurement deviates from room temperature significantly, then corrections should be made to the thermodynamic values obtained to adjust them to the desired thermodynamic temperature. Equilibria can also be established at low pressure, typically using an ion cyclotron resonance mass spectrometer (ICR-MS), but now the association reaction noted above is rarely observed.⁴⁶ Rather exchange equilibria are often examined, i.e., $ML_A^+ + L_B \leftrightarrow ML_B^+ + L_A$. As a consequence, this low-pressure approach usually yields relative thermochemistry that requires anchoring to some absolute $M^+ - L$ bond energy.

II.G. Photoionization Threshold (I)

In a photoionization (PI) experiment, neutral molecules are irradiated with photons of sufficient energy to induce ionization and dissociation.⁴⁷ By measuring the difference in the appearance energies (AEs) for the parent ion and its fragment (or between subsequent fragments), the BDE for this dissociation can be obtained. By using photons, the energy absorbed by the molecule is very well-known and sharp, in contrast to the broad distributions of collision-based experiments. The accurate extraction of thermodynamic information requires information about the energy content of the neutral molecule under study, and appearance energies of fragments can be shifted by the kinetics of dissociation. As discussed below, such experiments were not always corrected for the internal energy content of the neutral precursor and kinetic corrections are rare.

II.H. Kinetic Method (K)

Cooks and co-workers originally implemented the kinetic method (KM) as a simple means to estimate thermodynamic values from easily performed experiments,^{48,49} namely the relative intensities of products resulting from dissociation of a ion bound dimer, $(A)I^+(B)$, dissociating to $I^+(A) + B$ and $I^+(B) + A$.⁵⁰ The ratio of these intensities is presumed to rely primarily on the relative thermodynamics for the two product channels. Initially, the KM ignored entropic effects in the two product channels, but revisions in this initial approach now try to include them by examining the dissociation under several different excitation conditions (the so-called "extended kinetic method",⁵¹ which needs to be analyzed properly to avoid covariance in the data⁵²). Even here it is generally assumed that differences in entropies of the references can be ignored, which is never true in detail, although such entropies can be incorporated in the analysis.⁵⁰ Probably the primary limitation of the KM approach is that the temperature of the evaluation is ill-defined (and undoubtedly not Maxwellian). As a conse-

quence, it has seen extensive discussion concerning its utility and potential difficulties.^{53–56} It provides only relative values, and hence the accuracy of the determinations is ultimately limited by the reference data used to anchor the values obtained. As will be seen below, it has been utilized heavily and should provide useful relative information in the absence of more definitive data, although the precision of the relative values is probably overstated in many cases given the failure to consider all possible sources of experimental uncertainty.

II.I. Ion Mobility (M)

In ion mobility studies, ions are dragged through a viscous medium (usually He and more recently N_2) by an electric field.^{57–59} The rate at which the ions move in this environment depends on their interaction cross section with the gas, such that larger ions move more slowly than compact ions. In its simplest form (one commonly used today), the mobility of an ion measured under specific conditions is compared with that predicted by theory, thereby allowing the size and sometimes the shape of the ion to be assessed. Thermodynamic data can be obtained by acquiring mobility data as a function of E/N , the ratio of the electric field intensity to the neutral gas number density. For simpler systems, e.g., ions interacting with rare gases (Rg), model potentials for the interaction can be used to reproduce these mobility data, if such data are acquired over a sufficient range, thereby probing the full potential curve for the $M^+ - Rg$ interaction (i.e., both long-range and short-range interactions).^{60,61} Such "inversion" procedures are very sensitive to the assumptions made regarding the model potential used.⁶²

II.J. Photodissociation (P)

In a photodissociation (PD) experiment,⁶³ ions are exposed to light of a known frequency, which is varied until the onset for dissociation to products is observed. This onset is generally equated with the BDE of interest. As for photoionization, the main advantage of PD is that the photon energy is generally known extremely well (although exceptions include early experiments that utilized broad band light sources coupled with cutoff filters) and has no appreciable distribution. A primary disadvantage of photodissociation is that there is no way to know for sure whether the molecule of interest actually absorbs the photon at the BDE, such that the onset of dissociation may correlate with the beginning of an allowed transition, rather than a thermochemical result. Like collision-based experiments, the accurate extraction of thermodynamic information requires information about the energy content of the molecule under study and can be subject to the same kinetic shift issues. In some cases, detailed knowledge of the internal energy content of the reactant ions is not available, such that the photodissociation onset can be lower than the true thermodynamic threshold.

II.K. Ion–Molecule Reaction Bracketing (R)

When equilibrium cannot be established, rough experimental thermodynamic information can be obtained by noting whether a reaction (generally a ligand exchange process) occurs or not.⁶⁴ Observation of a reaction is generally assumed to indicate that the process is exothermic, whereas failure to observe a reaction is attributed to an endothermic process. The former assumption can be in error if the reaction observed is inefficient. The latter assumption is more problematic as failure to observe reactions can occur as a result of kinetic as well as

thermodynamic effects. Few results in the tables below rely on this relatively imprecise method.

II.L. Scattering (S)

In the scattering method for determining interaction potentials,⁶⁵ a beam of one species is collided with another species (either in a collision cell or another molecular beam). Differential cross sections (intensity of the scattered species as a function of the deflection angle) are measured, potentially as a function of the collision energy. Such differential cross sections are sensitive to the intermolecular potential, with low-energy collisions being most sensitive to the attractive part of the potential and high-energy collisions relating to the repulsive part. As for mobility data, the differential cross sections cannot be inverted directly to obtain the interaction potential, so model potentials are used to reproduce the data, either using assumed long-range attractive and short-range repulsive components or more flexible models.⁶⁶

II.M. Threshold of Endothermic Reaction (T)

Like ion–molecule reaction bracketing, this method is utilized to examine ligand exchange reactions when applied to noncovalent interactions (but has also been heavily used for the determination of many covalent bonding interactions).^{10,67,68} This approach has many similarities (including instrumentation) to the TCID method discussed above (section II.C). When the reaction of interest is endothermic, it can be driven by accelerating the ions to a known kinetic energy and determining its energy threshold. To acquire accurate thermodynamic information, the determination of the threshold requires that all sources of energy (kinetic and internal) and their distributions be accounted for and that various kinetic and entropic effects be included.

III. SYSTEMS

In the following tables, bond dissociation energies (BDEs) in kilojoules per mole are provided for reaction 1.



Values are provided at 0 K (roman) whenever available and at 298 K (in italics) and sometimes at an unspecified temperature. When conversion factors between 0 and 298 K are available in the literature (generally from calculations), values originally reported at 298 K have been adjusted to 0 K values here. Notations about such corrections are generally made, but may have been missed in some cases. Except for the very weakest BDEs (below about 10 kJ/mol), we have chosen to report all values to the nearest kilojoule per mole, consistent with the uncertainties in most values. Values are often reported more precisely in the original publications, and the reader should consult these for detailed values. In the tables below, we report BDEs for systems where comparisons can be made among several metals. We have chosen not to include values for ligands where thermochemistry for only a single metal is available (notably lithium). These can generally be found in the reviews noted above. Although we have attempted to be comprehensive in this compilation, omissions are inevitable.

In all tables, we augment the citations by noting the type of experiment that was used to determine the value. For this purpose, the one-letter codes introduced above are adopted here.

III.A. Rare Gases

Table 1 lists BDEs for interaction between various metal cations and the rare gases (Rg). Most of these data were acquired using mobility^{60–62,69–73} or scattering^{66,74–76} techniques. Among these data, Takebe has reported well depths for most of the alkali cation–rare gas interactions,⁶⁹ but in many cases, these values are considerably higher than those obtained from alternate sources. Reasons for these differences have been commented on by Viehland.⁶⁰ As a consequence, Table 1 does not include values from Takebe except in cases where they lie within the range determined elsewhere. Most measurements refer to a single ligand, although high-pressure temperature-dependent equilibrium studies (H) have measured values for one to three He and one and two Ne ligands.⁷⁷ In a few cases, values are obtained by examining the kinetic energy dependence of ligand exchange reactions in threshold of endothermic reaction experiments (T),^{78–83} and photodissociation measurements (P) contribute values for Mg⁺ and Al⁺.^{84,85} For Li⁺(Ar) and K⁺(Ar), we report the average value listed in the NIST Webbook,⁸⁶ and for several other cases, we list the average value taken from several references either listed in Table 1 or previously compiled.⁷⁶ One additional value not included in Table 1 is D₀(Pt⁺–Xe) = 83 ± 29 kJ/mol from threshold experiments (T).⁸⁷

The values in Table 1 reflect several periodic trends that are also evident in many of the following tables. Because the data here for metals other than the alkalis is incomplete, an examination of these species is deferred. At long range, the interaction potential between an alkali cation and a rare gas must be the ion-induced dipole potential, which is proportional to the polarizability of the rare gas. This is illustrated by Figure 1, which shows the BDE (or potential well depth) versus the polarizability volume of the rare gases for four of the alkali cations (values for Rb⁺ lie between those for K⁺ and Cs⁺).⁸⁸ For any individual cation, the BDEs clearly increase with polarizability, although the increase is not linear. This simply reflects the fact that the well depth is not simply related to the long-range potential. Indeed, the model potential most often used in describing these interactions combines the attractive r^{-4} dependence of the ion-induced dipole potential with an attractive r^{-6} dependence and a r^{-p} repulsion (where $p = 8$ –16 typically). In this regard, it can be remembered that these MRg⁺ complexes are isoelectronic with alkali halogen neutrals, such that there is substantial ionic character in the interaction.

Figure 1 also shows that the smaller cations bind more tightly than large cations. This is a clear electrostatic effect, in that the expected potential is greater for shorter internuclear distances. A more quantitative illustration of this effect is shown in Figure 2, where the BDEs are plotted versus the square of the metal cation radius, r .⁸⁹ It can be seen that the BDEs for a particular rare gas increase nearly linearly on these plots and additionally have intercepts close to zero (within 5 kJ/mol). Similar plots versus r^{-1} or r^{-4} show a similar correlation, but the former has a distinct increasing slope as r^{-1} increases and the latter has a decreasing slope as r^{-4} increases. Again this reflects the fact that the BDE is a complex mixture of long-range attractions along with both covalency and ionic character at the bottom of the potential well.

III.B. Small Molecules (H₂, NH₃, CO, CS, H₂O, CH₃CN)

III.B.1. H₂. Table 2 lists bond energies for many metal cations (including all first-row transition metals) with dihydrogen and includes values up to seven H₂ ligands.

Table 1. Bond Dissociation Energies (kJ/mol) of (Rg)_xM⁺–Rg for Rare Gas Ligands at 0 K^a

Rg	x	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ⁺	Al ⁺	Cr ⁺	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺
He	1	6.9 (0.3) ^b 4.5 ⁶¹	4.3 (1.3) ^{60,61,69}	2.3 (0.1) ^{60,66,69} 2.4 (0.5) ⁶²		1.4 (0.2) ^{61,74}			4.1 (0.4) ⁷⁷		12.6 (0.2) ⁷⁷	12.4 (0.2) ⁷⁷	
	2												
	3												
Ne	1	11.7 (0.4) ^b	6.2 (0.2) ^{60,69}	4.1 (0.4) ^{60,66,69}	3.2 ⁶⁰	2.5 (0.3) ^{69,74} 2.6 (0.6) ⁶²			5.8 (0.4) ⁷⁷		13.4 (0.4) ⁷⁷ 5.1 (0.4) ⁷⁷ 9.2 (0.4) ⁷⁷	13.4 (0.4) ⁷⁷ 5.6 (0.4) ⁷⁷ 9.9 (0.4) ⁷⁷ 3.1 (0.9) ^{77,c}	
	2								4.7 (0.9) ⁷⁷		8.7 (0.4) ⁷⁷	9.5 (0.4) ⁷⁷	
Ar	1	30 (6) ^b 30 (4) ⁸⁶ 33 (14) ⁷⁸ 27 ⁷²	15 (8) ⁷⁸ 11 ⁷⁵ 18 ⁶⁰ 20 ⁶⁹	12 (3) ⁸⁶ 14 (7) ⁷⁸	10 (2) ^{60,69,70}	8 (1) ^{60,69,71,74}	15 ⁸⁴ 10 (7) ⁸¹	12 (1) ⁸⁵	27 (2) ⁷⁷	11 (8) ⁷⁹			48 (7) ⁸⁰
	2												
	3												
Kr	1	41 (7) ^b	16 ⁷⁵ 21 ⁶⁰ 26 (2) ^{60,75}	13 (3) ^{60,66,69,73,75} 18 (3) ^{60,66,69,73,75}	12 (1) ^{60,61,69,70} 15 (3) ^{60,69,70}	11 (1) ^{60,69,71,74} 12 (2) ^{60,61,69,71,74}		18 (1) ⁸⁵		30 (7) ⁷⁹ 42 (6) ⁷⁹ 45 (8) ⁸³ 46 (8) ^d	82 (7) ⁸²		98 (6) ⁸⁰
Xe	1	51 (6) ^b					31 (12) ⁸¹						

^aUncertainties in parentheses. Multiple references refer to the average from all listed references. E = single temperature equilibrium,¹⁹⁵ H = high-pressure temperature-dependent equilibrium,⁷⁷ M = mobility,^{60–62,69–73} P = photodissociation and ionization,^{84,85} S = scattering,^{66,74,75} and T = threshold of endothermic reaction.^{78–83} ^bAverage of values from multiple experiments listed in ref 76. ^cCorresponds to an excited electronic state of Ni⁺. ^dRelative free energy (E)¹⁹⁵ anchored to D(Fe⁺–CH₄) from ref 161 and adjusted to 0 K in ref 79.

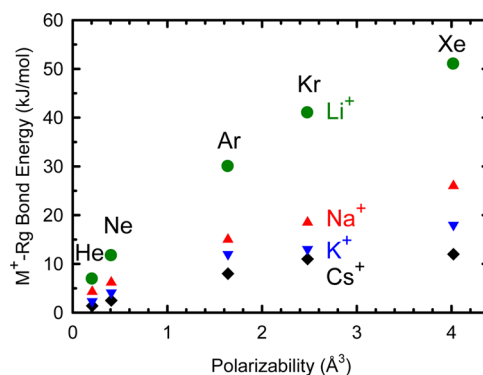


Figure 1. Alkali metal cation bond dissociation energies to rare gases as a function of the polarizability of the rare gas.

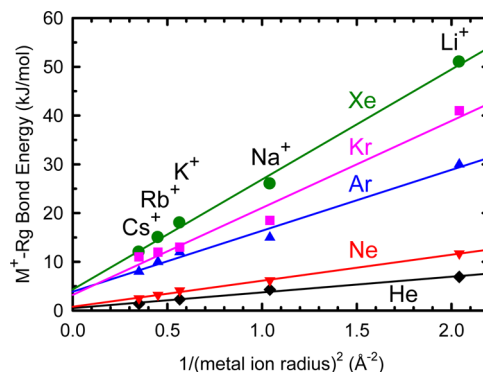


Figure 2. Alkali metal cation bond dissociation energies to rare gases as a function of the inverse square of the metal cation radius. Lines are linear regression fits to the data for each rare gas.

These are obtained primarily using high pressure temperature-dependent equilibrium studies (H) by Bowers and co-workers,^{90–101} with the value for Li⁺(H₂) coming from Wu.¹⁰² A single TCID experiment yields a BDE for Co⁺(H₂) in good agreement with the Bowers value.¹⁰³ Additional values are also available for (H₂O)V⁺(H₂)_x where x = 1–3, and for (H₂O)₂V⁺(H₂).⁹⁴ Notably H₂ binds perpendicularly to metal ions because of the sign of its quadrupole.

III.B.2. NH₃. Table 3 lists sequential BDEs for metal cations bound to ammonia. Most values come from TCID experiments (C), with the most comprehensive studies including those for potassium (x = 1–5),⁴² magnesium (x = 1–5),⁸¹ the first-row transition metals (x = 1–4),¹⁰⁴ and platinum (x = 1–4).¹⁰⁵ Values from early TCID experiments are also available for potassium and many of the transition metals,¹⁰⁶ and three laboratories have measured D(Na⁺–NH₃)^{106–108} and one D(Ag⁺–NH₃).¹⁰⁸ It can be seen that the agreement between the TCID values for the transition metals is reasonable and within the combined experimental uncertainties, although deviations up to 26 kJ/mol are observed. High pressure temperature-dependent equilibrium studies (H) provide values for lithium (x = 2–6),¹⁰⁹ sodium (x = 1–6),¹⁰⁹ potassium (x = 1–4),^{110,111} rubidium (x = 1–5),¹¹⁰ copper (x = 3–5),¹¹² silver (x = 2–4),¹¹² and bismuth (x = 1–3).¹¹⁰ Agreement between these equilibrium values and those from TCID experiments are again reasonable (see, for example, potassium, x = 1–4). Equilibrium studies using ICR methods have provided D(Li⁺–NH₃),^{12,113,114} D(Na⁺–NH₃),^{115,116} and D(Mn⁺–NH₃).¹¹⁷ These latter values depend on how the relative scales are anchored and adjusted from free energies to the enthalpies

Table 2. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{H}_2)_{x-1}\text{M}^+-\text{H}_2$ at 0 K^a

M ⁺	ref ^b	x = 1	x = 2	x = 3	x = 4	x = 5	x = 6	x = 7
Li ⁺	H ¹⁰²	27 (35)						
Na ⁺	H ⁹⁰	10 (1)	9 (1)					
K ⁺	H ⁹⁰	6 (1)	5 (2)					
Al ⁺	H ⁹¹	6 (1)	5 (1)					
Sc ⁺	H ⁹²	23 (1)	27 (2)	23 (1)	21 (2)	~18		
Ti ⁺	H ⁹³	31 (2)	41 (3)	39 (3)	36 (2)	34 (2)	36 (2)	
V ⁺	H ⁹⁴	43 (2)	45 (2)	37 (2)	38 (2)	18 (2)	40 (2)	<8
Cr ⁺	H ⁹⁵	32 (2)	37 (2)	20 (2)	14 (2)	6 (2)	5 (2)	
Mn ⁺	H ⁹⁶	8 (2)	7 (2)	~6	~5			
Fe ⁺	H ⁹⁷	45 (3)	66 (3)	31 (2)	36 (2)	9 (1)	10 (1)	
Co ⁺	H ⁹⁸	76 (4)	71 (3)	40 (2)	40 (2)	18 (3)	17 (3)	3–7
	C ¹⁰³	73 (10)						
Ni ⁺	H ⁹⁹	72 (1)	74 (1)	47 (1)	30 (1)	18 (1)		
Cu ⁺ (d ¹⁰)	H ¹⁰⁰	64 (4)	70 (4)	37 (2)	21 (2)	4 (1)	4 (1)	
Cu ⁺ (s ¹ d ⁹)	H ¹⁰⁰	18 (1)	10 (2)	6 (1)				
Zn ⁺	H ⁹⁶	16 (2)	12 (2)	10 (2)	7 (2)	6 (2)	~6	
Zr ⁺	H ¹⁰¹	61 (1)	45 (1)	42 (1)	38 (2)	38 (2)	37 (3)	36 (3)

^aUncertainties in parentheses. ^bC = threshold collision-induced dissociation. H = high-pressure temperature-dependent equilibrium.

Table 3. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{NH}_3)_{x-1}\text{M}^+-\text{NH}_3$ ^a

M ⁺	ref ^b	x = 1	x = 2	x = 3	x = 4	x = 5	x = 6
Li ⁺	H ¹⁰⁹	159 (10) ^c	138 (5)	88 (1)	69 (1)	46 (1)	39 (3)
	E ^d	158 (15)					
	C ³⁶⁴	166 (9)					
Na ⁺	H ¹⁰⁹	118 (2)	96 (1)	72 (1)	62 (1)	45 (1)	41 (1)
	C ¹⁰⁷	102 (5)					
	H ^{115,116e}	103 (1)					
	C ¹⁰⁶	115 (19)					
	C ¹⁰⁸	107 (12)					
K ⁺	H ¹¹⁰	81 (5)	68 (5)	56 (4)	49 (4)		
	C ⁴²	79 (4)	69 (3)	59 (3)	46 (3)	31 (6)	
	H ¹¹¹	71 (4)					
	C ¹⁰⁶	71 (19)					
Rb ⁺	H ¹¹⁰	78	64	55	48	43	
Mg ⁺	C ⁸¹	154 (12)	123 (7)	96 (9)	43 (11)	56 (12)	
Ti ⁺	C ¹⁰⁴	195 (7)	175 (17)	176 (18)	156 (10)		
V ⁺	C ¹⁰⁴	190 (11)	164 (9)	104 (11)	95 (11)		
	C ¹⁰⁶	215 (19)	188 (19)	89 (19)	74 (19)		
Cr ⁺	C ¹⁰⁴	182 (10)	179 (9)	54 (6)	30 (9)		
	C ¹⁰⁶	156 (19)	171 (19)				
Mn ⁺	C ¹⁰⁴	147 (8)	152 (12)	64 (10)	36 (6)		
	C ¹⁰⁶	154 (19)	142 (19)	47 (19)			
	E ^{117f}	136 (10)					
Fe ⁺	C ¹⁰⁴	183 (12)	224 (11)	68 (15)	42 (7)		
	C ¹⁰⁶	160 (19)	201 (19)				
Co ⁺	C ¹⁰⁴	218 (16)	249 (11)	64 (6)	49 (6)		
	C ¹⁰⁶	245 (19)	254 (19)				
Ni ⁺	C ¹⁰⁴	231 (19)	249 (13)	90 (8)	37 (6)		
	C ¹⁰⁶	214 (19)	228 (19)	71 (19)			
Cu ⁺	C ¹⁰⁴	237 (15)	246 (10)	47 (6)	42 (6)		
	H ¹¹²			58 (1) ^g	51 (1) ^g	54 (1)	
Ag ⁺	H ¹¹²	170 (13) ^{108C}	154 (3)	61 (1)	54 (1)	54 (1)	
Pt ⁺	C ¹⁰⁵	274 (12)	261 (10)	77 (5)	46 (4)		
Bi ⁺	H ¹¹⁰	149	97	56			

^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. ^bReference for this row except as noted. C = threshold collision-induced dissociation. E = single temperature equilibrium. H = high-pressure temperature-dependent equilibrium. ^cFrom ICR equilibrium (E) at 373 K.^{12,113} Adjusted to 0 K in ref 196. ^dFrom ICR equilibrium (E) at 298 K.¹¹⁴ Reanchored and adjusted to 0 K in ref 196. ^eAdjusted to 0 K using information in ref 107. ^fFrom ICR equilibrium (E) at presumed 298 K.¹¹⁷ Adjusted from relative free energies by symmetry number only. Anchored here to value for Mn⁺(C₆H₆) from Table 20. ^gAdjusted to 0 K using information in ref 104.

Table 4. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{CO})_{x-1}\text{M}^+-\text{CO}$ at 0 K^a

M ⁺	ref ^b	x = 1	x = 2	x = 3	x = 4	x = 5	x = 6	x = 7
Li ⁺	C ⁷⁸	55 (13)	36 (4)	35 (4)				
Na ⁺	C ⁷⁸	32 (8)	24 (3)					
	H ^{128c}	55	34					
Mg ⁺	C ⁸¹	42 (6)	39 (3)					
K ⁺	C ⁷⁸	18 (5)						
Ti ⁺	C ¹²⁰	118 (6)	113 (4)	100 (4)	87 (5)	70 (4)	74 (3)	52 (7)
V ⁺	C ¹²¹	113 (3)	91 (4)	70 (4)	86 (10)	91 (3)	99 (7)	50 (9)
Cr ⁺	C ¹²²	90 (4)	94 (3)	54 (6)	51 (8)	62 (3)	130 (8)	
Mn ⁺	C ¹²³	25 (10)	63 (10)	74 (10)	65 (10)	121 (10)	142 (10)	
	D ^{44d}	>29	<105	130 (25)	84 (13)	67 (13)	134 (21)	
Fe ⁺	C ^{30e}	129 (8) [153] ^f	148 (5)	69 (6)	98 (6)	97 (4)		
	I ¹²⁹	132 (14) ^g [154] ^f	169 (14) ^g	78 (14)	106 (14)	101 (10) [76] ⁱ		
	I ¹³⁰	142 (8) [164] ^f	174 (7)	108 (6)	105 (5)	99 (4) [74] ⁱ		
	K ^{133h}	131 (11)						
Co ⁺	C ¹²⁴	174 (7)	153 (9)	82 (12)	75 (6)	75 (5)		
	D ¹²⁵	164 (13)						
Ni ⁺	C ¹²⁶	175 (11)	168 (11)	92 (6)	72 (3)			
	I ¹²⁹	183 (14)	150 (14)	128 (10)	68 (2) [43] ⁱ			
Cu ⁺	C ¹²⁷	149 (7)	172 (3)	75 (4)	53 (3)			
Ag ⁺	C ¹²⁷	89 (5)	109 (4)	55 (8)	45 (4)			
Pt ⁺	C ⁸⁷	212 (10)	193 (10)	98 (5)	53 (5)			

^aUncertainties in parentheses. ^bC = threshold collision-induced dissociation, D = kinetic energy release distribution (KERD), H = high-pressure temperature-dependent equilibrium, I = photoionization threshold, and K = kinetic method. ^cAdjusted to 0 K using information in ref 78. See discussion in section III.B.2. ^dKERD (D) values that depend on assumptions for preexponential A factors. ^eReevaluated in ref 83. ^fValues in brackets are uncorrected for the possibility that dissociation correlates with $\text{Fe}^+(\text{F}) + \text{CO}$ products. ^gValues adjusted in ref 132. ^hRelative value from kinetic method (K) ¹³³ anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ from ref 135. ⁱValues in brackets are uncorrected for the approximate thermal energy content of neutral precursor, 25 kJ/mol. ¹²⁶

reported here, as described in the table footnotes. Note that the latter $D(\text{Mn}^+-\text{NH}_3)$ value has been anchored here to the $D(\text{Mn}^+-\text{C}_6\text{H}_6)$ BDE reported in Table 20. This scale could just as easily have been anchored to the $D(\text{Mn}^+-\text{NH}_3) = 147 \pm 8$ kJ/mol value,¹⁰⁴ uniformly raising these values by 11 kJ/mol.

The primary controversial value in Table 3 is $D(\text{Na}^+-\text{NH}_3)$, where there is excellent agreement between the TCID value¹⁰⁷ and the temperature dependent equilibrium value from McMahon,^{115,116} with both of these values lying considerably lower (and outside of the experimental uncertainties) than that reported by Castleman and co-workers, also from temperature dependent equilibrium studies.¹⁰⁹ Alternative TCID values lie within experimental uncertainty of both of these values.^{106,108} These results and those for several other ligands have been scrutinized elsewhere.¹¹⁸ For a wide range of ligands, TCID values and those from McMahon agree with each other and with several levels of theory, whereas the Castleman values are systematically higher (by 21 ± 10 kJ/mol compared to the TCID values).¹¹⁸ One possible explanation for this disparity was explored later by Gilligan et al.,¹¹⁹ who noted that the means used to produce Na^+ in these studies also formed Na metastables, which could enhance the production of the Na^+ -ligand complexes by associative ionization.

III.B.3. CO and CS. Table 4 lists sequential BDEs for carbon monoxide to many metal cations, most of which come from TCID studies.^{30,78,81,87,120–127} Values for sodium are also obtained by high pressure temperature-dependent equilibrium studies (see section III.B.2 for a discussion of such values).¹²⁸ It should also be realized that there are extensive sets of values available for the transition metal carbonyls from appearance energy (AE) measurements, using either electron ionization or photoionization. Table 4 does not include these values because

they are believed to be systematically in error. This has been demonstrated by comparing the sum of the BDEs $[\text{M}^+(\text{CO})_x \rightarrow \text{M}^+ + x\text{CO}]$ to the value calculated from the enthalpy of formation of the $\text{M}(\text{CO})_x$ precursor, its ionization energy, and the enthalpies of formation of M^+ and CO. Using $\text{Cr}(\text{CO})_6^+$ as an example, as detailed elsewhere,¹²² this thermodynamic cycle indicates that the six carbonyl BDEs should sum to 487 ± 9 kJ/mol. The TCID values listed in Table 4 sum to 481 ± 14 kJ/mol, within experimental uncertainty, whereas various AE measurements differ from the expected value by 124 ± 14 , 134 ± 21 , 165 ± 10 , and 64 ± 15 kJ/mol.

Table 4 does include values from arguably the best two photoionization studies (I),^{129,130} which are also illustrative. For $\text{Ni}(\text{CO})_4^+$, the thermodynamic cycle indicates the sum of BDEs is 517 ± 14 kJ/mol, compared with 507 ± 17 kJ for the TCID results¹²⁶ and 529 ± 10 kJ/mol from PI¹²⁹ (505 ± 10 kJ/mol if a 25 kJ/mol correction¹²⁶ for the internal energy of the $\text{Ni}(\text{CO})_4$ precursor is not included). Oddly, Distefano corrects only the Ni^+ onset for this internal energy (which he estimated at 19 kJ/mol) instead of all appearance energies, even though such internal energy must affect all thresholds except for the ionization energy measurement. Relative AE values properly corrected lead to the BDEs listed in Table 4 and can be seen to agree reasonably well with those directly measured using TCID methods. (Note that values for $x = 2$ and 3 are unaffected by whether this correction is made or not, but the value for $x = 4$ increases and that for $x = 1$ decreases. When corrected, the latter two values agree much better with the TCID results.)

For iron pentacarbonyl, similar considerations hold and the values from the PI studies for $(\text{CO})_4\text{Fe}^+-\text{CO}$ agree much better with the TCID result when the former are corrected for the internal energy of the precursor (again estimated at 25 kJ/

Table 5. Bond Dissociation Energies (kJ/mol) of M^+-CX , Where $X = O$ and S for First- and Second-Row Transition Metals at 0 K^a

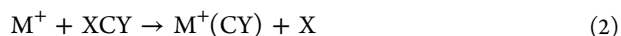
ligand	Sc ⁺	Ti ⁺	V ⁺	Cr ⁺	Mn ⁺	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺	Zn ⁺
CS	133 (8) ¹⁴²	154 (6) ¹⁴²	164 (8) ¹⁴⁰	163 (6) ¹⁴³	80 (21) ¹⁴³	232 (12) ¹⁴¹	259 (33) ¹⁴⁴	234 (10) ¹⁴⁵	238 (12) ¹⁴⁵	149 (23) ¹⁴⁵
ligand	Y ⁺	Zr ⁺	Nb ⁺	Mo ⁺	Tc ⁺	Ru ⁺	Rh ⁺	Pd ⁺	Ag ⁺	Cd ⁺
CO	30 (11) ¹³⁸	77 (10) ¹³⁹	96 (5) ¹³⁷	>44 (16) ¹³⁶					89 (5) ¹²⁷	
CS	137 (8) ¹⁴⁷	258 (11) ¹⁴⁷	242 (11) ¹⁴⁷	162 (14) ¹⁴⁶		250 (17) ¹⁵¹	257 (18) ¹⁴⁸	258 (20) ¹⁴⁹	191 (14) ¹⁵⁰	

^aUncertainties in parentheses. All values measured from thresholds of endothermic reactions (T) except $D(\text{Ag}^+-\text{CO})$ (C).¹²⁷

mol). An additional complication in the iron system is the possibility that the FeCO^+ species may dissociate to an excited state asymptote (yielding a value above the adiabatic BDE). Calculations indicate that FeCO^+ has a quartet ground state,¹³¹ whereas Fe^+ has a sextet ground state with its quartet state lying 22 kJ/mol higher in energy. Values in Table 4 are listed for both possibilities, but the sum of the TCID BDEs for the lower value (564 ± 13 kJ/mol) agrees slightly better with the value from the literature thermodynamic cycle (571 ± 8 kJ/mol). Note that the PI studies yield BDE sums of 586 ± 10 kJ/mol¹²⁹ and 628 ± 13 kJ/mol¹³⁰ (after correcting for the diabatic dissociation and including adjustments discussed elsewhere¹³²).

Additional values from other sources include those for $\text{Mn}^+(\text{CO})_x$ for $x = 1-6$,⁴⁴ $\text{Fe}^+(\text{CO})$,¹³³ and $\text{Co}^+(\text{CO})$.¹²⁵ Values listed for $\text{Mn}^+(\text{CO})_x$ were obtained by a speculative analysis of kinetic energy release distribution (KERD, D) data for ions with a broad internal energy distribution, which necessitates assuming a value for the Arrhenius preexponential factor (A). As there is little guarantee that these assumptions are quantitatively correct, a rigorous evaluation of the activation energy for dissociation in these experiments is suspect. In contrast, the KERD study for decarbonylation of acetone by Co^+ utilizes precursor ions with well-defined internal energies, such that the analysis can lead to reasonable values (although notably, this work discounts a previous analysis of the same decomposition yielding 142 ± 13 kJ/mol¹³⁴). Finally, the kinetic method (K) was used to evaluate the relative energies of Fe^+ bound to several small molecules, using $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ ¹³⁵ as an absolute anchor. In these experiments, because the reactions never produce the atomic ion, all species remain as quartets. Thus, the good agreement between this value and those from the TCID and PI experiments is another indication that the correction for diabatic dissociation is appropriate.

In addition to the values in Table 4, Table 5 lists metal carbonyl cation BDEs for several of the second-row transition metal series along with metal thiocarbonyl cation BDEs for both first- and second-row transition metals. With the exception of $D(\text{Ag}^+-\text{CO})$, which is a TCID value,¹²⁷ all values in Table 5 are measured by determining the threshold for the endothermic reaction 2 (T)



(where X and Y = O or S).¹³⁶⁻¹⁵¹ In the CO_2 studies with Y^+ , Zr^+ , Nb^+ , and Mo^+ ,¹³⁶⁻¹³⁹ BDEs for OM^+-CO , $\text{O}_2\text{M}^+-\text{CO}$, and OM^+-CO_2 were also measured but are not listed.

III.B.4. H_2O . Not surprisingly, measurements of hydration energies are among the most extensively studied ligand systems, and as a consequence the values are listed in three separate tables. Table 6 provides the inner solvation shell for singly charged metal ions; Table 7 has the same information for doubly charged metal ions; and Table 8 contains information for larger complexes (up to 14 water ligands) primarily for doubly charged metal cations but including values for Sr^+ . For

the alkali cations, most values are from high pressure temperature-dependent equilibrium studies (H),^{152,153} although TCID values (C) for Li^+ and Na^+ are also available^{39,40} and in reasonable agreement. Notably, the equilibrium studies could not access the strongly bound $\text{Li}^+(\text{H}_2\text{O})$ system, but absolute TCID measurements and relative values from ICR equilibrium studies (E) provide similar values. Additional values are provided by an infrared photodissociation method (P) (which probably has appreciable uncertainties associated with the unknown ion temperature),¹⁵⁴ temperature dependent flame calorimetry (which also provides values for CaOH^+ and SrOH^+),¹⁵⁵ and mobility measurements (M) of the hydration of Cs^+ .¹⁵⁶ Table 6 also includes values from Kebarle and co-workers (H) for potassium that have been corrected for unimolecular dissociation.¹⁵⁷ It can be seen that this correction drops the reported hydration enthalpies by as much as 7 kJ/mol. Such a correction is probably needed on a routine basis, but its application is not always made clear in the literature.

Hydration enthalpies for Mg^+ and Al^+ are also available from TCID studies (C),³⁹ along with one photodissociation (P) value for $\text{Mg}^+(\text{H}_2\text{O})$.¹⁵⁸ High pressure temperature-dependent equilibrium (H) values for Ca^+ ($x = 1-5$) are also available (although few experimental details are provided).¹⁵⁹ Hydration of the first-row transition metal cations is one of the first systems to be systematically evaluated using TCID methods.^{106,160} In these early studies, not all effects were included in the data analysis, such that the more recent and comprehensive TCID studies probably supplant these values.^{38,161} Nevertheless, there is generally good agreement among all three studies. Hydration of CuOH^+ has also recently been studied using TCID methods.¹⁶² For heavier metals, high pressure temperature-dependent equilibria (H) have been used to determine hydration enthalpies for Ag^+ ($x = 1-6$),¹¹² Sr^+ ($x = 1-9$),¹⁶³ Pb^+ ($x = 1-6$),¹⁶⁴ and Bi^+ ($x = 1-6$).¹⁶⁵ TCID values for Ag^+ are in reasonably good agreement with the equilibrium values.^{166,167} It should be mentioned that the values for Sr^+ seem exceptionally large, actually exceeding that for Li^+ . With an ion radius of 1.44 Å, one imagines these values should be somewhat less than those for K^+ ($r = 1.33$ Å) and Ag^+ ($r = 1.13$ Å),⁸⁹ although other factors could alter this simple expectation (see discussion below). Theoretical results for the $x = 1-3$ complexes predict values that are about 2/3 of the experimental values listed.¹⁶⁸

Tables 7 and 8 include hydration enthalpies for the metal dications for both inner shell (defined here loosely as $x = 1-6$) and outer shell ($x \geq 7$). For the smaller complexes, the values are obtained exclusively using TCID methods (C),¹⁶⁹⁻¹⁷⁸ because equilibrium methods cannot access sufficiently high temperatures to establish equilibrium for such strong bonds. (In the case of Zn^{2+} , slightly different values are obtained depending on which level of theory is used to ascertain the lowest energy structures used for modeling of the TCID

Table 6. Sequential Bond Dissociation Energies (kJ/mol) of (H₂O)_{x-1}M⁺–H₂O for $x = 1-6^a$

M ⁺	ref ^b	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
Li ⁺	C ⁴⁰	135 (8) ^{9,34,40c}	113 (10)	94 (4)	70 (5)	57 (4)	60 (5)
	H ^{152d}	133 (14) ^{40,196}	107 (4)	87 (4)	68 (4)	55 (4)	48 (4)
	E	134 (10) ^e				53 (3) ^{154p}	
	E	137 (14) ^f					
	E	139 (15) ^g					
Na ⁺	H ¹⁵²	97 (4)	80 (4)	63 (4)	58 (4)	51 (4)	45 (4)
	C ³⁹	95 (8)	82 (6)	70 (6)	55 (6)		
	H ¹⁶³	88 (6) ^{107C}		59	51	44	
	H ¹⁶⁴	84 (18) ^{106C}			55	49	
	P ¹⁵⁴	98 (10) ^h		~50	51 (2)	49 (3)	
K ⁺	H ^{152,153}	75 (4)	67 (4)	55 (4)	49 (4)	45 (4)	42 (4)
	H ¹⁵⁷	71 ^{111,157}	67	54	46	40	35
	P ¹⁵⁴	71 (10) ^h		46 (3)	48 (4)	<45	
Rb ⁺	H ¹⁵²	67 (4)	57 (4)	51 (4)	47 (4)	44 (4)	
		67 (10) ^h					
Cs ⁺	H ¹⁵²	57 (4)	52 (4)	47 (4)	44 (4)		
	M ¹⁵⁶	50 (4)	47 (4)	41 (4)			
Mg ⁺	C ³⁹	119 (13)	94 (7)	72 (9)	48 (9)		
	P ¹⁵⁸	102					
Al ⁺	C ³⁹	104 (15)	67 (5)	64 (8)	52 (6)		
Ca ⁺	H ¹⁵⁹	117	100	90	78	73	
CaOH ⁺		134 (10) ^h					
Ti ⁺	C ³⁸	154 (6)	136 (5)	67 (7)	84 (8)		
	C ¹⁹²	156 (13)					
V ⁺	C ³⁸	147 (5)	151 (10)	68 (5)	68 (8)		
	C ¹⁰⁶	144 (17)	149 (17)	51 (17)			
	C ¹⁹²	148 (13)					
	C ³⁸	129 (9)	142 (6)	50 (5)	51 (7)		
Cr ⁺	C ¹⁰⁶	88 (17)	129 (17)				
	C ¹⁹²	118 (13)					
	C ³⁸	119 (6)	90 (5)	108 (6)	50 (5)		
	C ¹⁹²	108 (13)	74 (13)				
Mn ⁺	C ¹⁰⁶	116 (17)	72 (17)				
	C ¹⁶¹ⁱ	128 (5)	164 (4)	76 (4)	50 (7)		
	C ¹⁹²	117 (13)	159 (13)				
	C ¹⁰⁶	134 (17)	170 (17)				
Co ⁺	K ^{133j}	129 (11)					
	C ³⁸	161 (6)	162 (7)	65 (5)	58 (6)		
	C ¹⁹²	152 (13)	188 (13)				
	C ¹⁰⁶	164 (17)	175 (17)				
Ni ⁺	C ³⁸	180 (3)	168 (8)	68 (6)	52 (6)		
	C ¹⁹²	149 (13)	159 (13)				
	C ¹⁰⁶	162 (17)	170 (17)				
Cu ⁺	C ³⁸	157 (8)	170 (7)	57 (8)	54 (4)		
	C ¹⁶⁰	143 (13)	163 (13)	71 (13)	63 (13)		
	H ¹¹²			70 (1)	69 (1)	59 (1)	
CuOH ⁺	C ¹⁶²	180 (5)	126 (8)	89 (3)	57 (6)		
Ag ⁺	C ¹⁶⁶	131 (8)	126 (8)	62 (10)	48 (12)		
	H ^{112k}	137 (9)	110 (2)	62 (2)	58 (2)	57 (1)	56 (3)
	C ¹⁶⁷	132 (11)					
Sr ⁺	H ¹⁶³	144	128	108	93	86	77
SrOH ⁺		115 (10) ^h					
Pb ⁺	H ¹⁶⁴	94	71	51	45	42	40
Bi ⁺	H ¹⁶⁵	95	74	59	50	44	41

^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. ^bReference for this row except as noted. C = threshold collision-induced dissociation, E = single temperature equilibrium, H = high-pressure temperature-dependent equilibrium, K = kinetic method, M = mobility, P = photodissociation. ^cReevaluated in ref 34. ^dUncertainties not specified, estimated as 4 kJ/mol. In some cases, values have been adjusted to 0 K in subsequent work. ^eFrom ICR equilibrium (E) at 373 K.^{12,113} Adjusted to 0 K in ref 196. ^fFrom ICR equilibrium (E) at 298 K.¹¹⁴ Reanchored and adjusted to 0 K in ref 196. ^gRelative free energy (E) from ICR equilibrium at 298 K,¹⁸⁷ reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. ^hFlame calorimetry over a temperature range of 1400–1800 K¹⁵⁵ and adjusted there

Table 6. continued

approximately to 298 K by subtracting 10 kJ/mol. ⁱReevaluated in ref 38. ^jRelative value from kinetic method (K)¹³³ anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ from ref 135. ^kValues from ref 112 adjusted to 298 and 0 K in ref 166.

Table 7. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{H}_2\text{O})_{x-1}\text{M}^{2+}-\text{H}_2\text{O}$ for $x = 1-6^a$

M ²⁺	ref ^b	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
Mg ²⁺	C ¹⁶⁹		256 (36)	226 (15)	178 (10)	116 (9)	97 (8)
	B ^{180,181}					107 (5)	98 (7)
	H ¹⁸²						100 (4)
Ca ²⁺	C ^{170,171}	247 (6)	199 (17)	171 (9)	142 (9)	114 (8)	101 (9)
	B ^{180,181}					110 (6)	90 (3)
	H ¹⁸²						104 (4)
Sr ²⁺	C ¹⁷²	201 (6)	172 (5)	144 (5)	124 (4)	103 (4)	94 (3)
	B ^{180,181}					100 (4)	86 (4)
	H ¹⁸²						94 (4)
Ba ²⁺	C ¹⁷³	169 (5)	145 (7)	129 (4)	107 (4)	92 (6)	77 (5)
	B ^{180,181}				107 (4)	88 (3)	75 (3)
	H ¹⁸²					99 (4)	82 (4)
Fe ²⁺	C ¹⁷⁴				167 (12)	108 (6)	95 (6)
Zn ²⁺	C ^{175c}						95 (4)
Cd ²⁺	C ^{176,177}			186 (14)	147 (4)	107 (5)	87 (5)

^aValues at 0 K. Uncertainties in parentheses. ^bReference for this row except as noted. B = blackbody infrared radiative dissociation, C = threshold collision-induced dissociation, and H = high-pressure temperature-dependent equilibrium. ^cValues interpreted on the basis of MP2(full) molecular parameters, see ref 179.

Table 8. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{H}_2\text{O})_{x-1}\text{M}^{n+}-\text{H}_2\text{O}$ for $x = 7-14^a$

M ⁿ⁺	ref ^b	$x = 7$	$x = 8$	$x = 9$	$x = 10$	$x = 11$	$x = 12$	$x = 13$	$x = 14$
Mg ²⁺	C ¹⁶⁹	70 (8)	67 (7)	59 (7)	44 (6)				
	B ^{180,181}	73 (5)	76 (8)	67 (6)	52 (4)				
	H ¹⁸²	82 (4)	71 (4)	67 (4)	65 (4)	60	54	51	51
Ca ²⁺	C ^{170,171}	60 (6)	59 (3)	58 (3)					
	B ^{180,181}	69 (5)	70 (5)	61 (6)	49 (6)				
	H ¹⁸²	67 (4)	63 (4)	60 (4)	61 (4)	56	54	52	50
Sr ²⁺	H ¹⁶³	72	69	56					
	H ¹⁸²	71 (4)	67	65	62	59	57	54	
	B ^{180,181}	70 (4)							
Ba ²⁺	H ¹⁸²	66 (4)	61 (4)	63 (4)	59	56	52	49	46
	C ¹⁷³	55 (6)	48 (9)						
	B ^{180,181}	64 (3)							
Mn ²⁺	E ^{183c}			64	63	61	59		
Fe ²⁺	C ¹⁷⁴	78 (5)	70 (7)	55 (4)	50 (6)	46 (4)			
Co ²⁺	E ^{183c}				64	61	59		
Ni ²⁺	E ^{184c}		63	63	62	60	60	59	
Cu ²⁺	C ¹⁷⁸	101 (3)	73 (4)	50 (6)	49 (7)				
Zn ²⁺	C ^{175d}	79 (5)	68 (6)	53 (8)	43 (3)				
Cd ²⁺	C ^{176,177}	68 (5)	64 (6)	59 (5)	47 (5)	42 (5)			

^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. ^bReference for this row except as noted. B = blackbody infrared radiative dissociation, C = threshold collision-induced dissociation, E = single temperature equilibrium, and H = high-pressure temperature-dependent equilibrium. ^cFree energies obtained from equilibrium data (E) are adjusted here to 300 K enthalpies by adding 29 kJ/mol, which assumes $\Delta S = 96 \text{ J/K mol}$ at 300 K. ^dValues interpreted on the basis of MP2(full) structures, see ref 179.

data.¹⁷⁵ Values cited here are those obtained using the MP2 structures as these have since been demonstrated by infrared multiple photon dissociation (IRMPD) action spectroscopy to predict these structures much more accurately.¹⁷⁹ For several metals (Mg, Fe, Cu, Zn, Cd), the smallest complexes cannot be generated easily in these studies because the $\text{M}^{2+}(\text{H}_2\text{O})_x$ complexes spontaneously decompose into $\text{MOH}^+(\text{H}_2\text{O})_{x-y-1} + \text{H}^+(\text{H}_2\text{O})_y$. Blackbody infrared radiative dissociation (BIRD, B) methods provide BDEs starting at about $x = 5$ and extending to $x = 10$.^{180,181} High pressure temperature-dependent

equilibria values (H) start about $x = 6$ and can extend out to $x = 14$.¹⁸²⁻¹⁸⁴ Reasonable agreement is obtained among all three methods, although for the largest complexes the TCID values tend to be somewhat smaller than the BIRD and equilibrium values. This could be because the complexes in the TCID studies are somewhat warmer than the assumed room temperature, because the equilibrium values do not include needed corrections for dissociation (see discussion above) and/or some cooling during the sampling process has occurred.¹⁵⁷

Table 9. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{CH}_3\text{CN})_{x-1}\text{M}^+-\text{CH}_3\text{CN}^a$

M^+	ref ^b	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
Li^+	E ^c	177 (15)					
Na^+	H ^{185d}	124 (6) ^d	102 (4)	86 (4)	62 (4)	53 (4)	
	C ¹⁹⁰	128 (5)	109 (8)	89 (3)	65 (3)	53 (4)	
	C ¹⁰⁸	126 (10)					
K^+	H ¹⁸⁵	102 (2)	86 (2)	76 (1)	57 (2)	48 (1)	
Rb^+	H ¹⁸⁵	87 (1)	74 (1)	66 (1)	52 (1)	46 (3)	
Cs^+	H ¹⁸⁵	80 (1)	70 (1)	60 (1)	51 (1)	46 (1)	
Al^+	H ¹⁸⁶	151 (11) ^e	93 (4)				
	E ^{15f}	152 (11)					
Fe^+	K ^{133g}	173 (11)					
Cu^+	C ¹⁹¹	238 (3)	238 (9)	84 (2)	67 (2)	60 (4)	46 (3)
Ag^+	C ²³⁶	162 (6)	145 (7)				

^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. ^bReference for this row except as noted. C = threshold collision-induced dissociation, E = single temperature equilibrium, H = high-pressure temperature-dependent equilibrium, and K = kinetic method. ^cRelative free energy (E) from ICR equilibrium at 298 K,¹⁸⁷ reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. ^dRelative free energy (E) from ICR equilibrium at 298 K¹¹⁶ adjusted to 0 K in ref 190. ^eRelative free energy (E) from ref 188 anchored as discussed in ref 186 and adjusted here from 298 to 0 K using information in ref 15. ^fRelative free energy (E) from refs 15 and 189 anchored here to $D(\text{Al}^+-\text{CH}_2\text{O})$ from ref 186 and adjusted to 0 K using information calculated in ref 15. ^gRelative free energy (E)¹³³ anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ from ref 135.

III.B.5. CH_3CN . Fewer studies have been performed for the acetonitrile ligand than for the other simple ligands, but there are still a considerable number of values available for the sequential BDEs to several metal cations as provided in Table 9. High pressure temperature-dependent equilibrium studies (H) by Kebarle and co-workers provide those for the heavier alkali cations¹⁸⁵ and for the second ligand on Al^+ .¹⁸⁶ Once anchored (as described in the Table 9 footnotes), single temperature equilibria (E) provide values for the first ligands to Li^+ and Al^+ .^{187–189} Relative values obtained using the kinetic method (K) and anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ ¹³⁵ yield the $\text{Fe}^+-\text{NCCH}_3$ BDE. Threshold collision-induced dissociation (C) has yielded sequential bond energies for $\text{Na}^+(\text{CH}_3\text{CN})_x$ for $x = 1–5$ and $\text{Cu}^+(\text{CH}_3\text{CN})_x$ for $x = 1–6$.^{108,190,191} The sodium system is essentially the only system where multiple methods have been used, and it can be seen that the equilibrium and TCID values are in good agreement.

III.B.6. Periodic Trends. Although all details that influence the periodic trends in these data cannot be reiterated here, several general observations can be made concerning the BDEs of Tables 2–9 that lead to several relevant concepts that control the relative ability of these metal cations to bind these ligands.

III.B.6.a. Metal Cation Size. Figure 3 shows the values for M^+-L BDEs of $\text{L} = \text{H}_2$, CO , H_2O , and NH_3 as a function of metal cation. As for the rare gases, BDEs to these ligands decrease as the alkali cation gets larger. In contrast, the transition metal cations generally bind more strongly than Li^+ (although there are several exceptions discussed below) even though they cannot have a smaller radius. Moving across the periodic table in the transition series, the orbital radii of the metal cations decrease because of the increasing nuclear charge. Thus, calculations indicate that the 3d orbital radius of Sc^+ is ~ 1.0 Å and this drops to ~ 0.5 Å by Cu^+ , whereas the 4s orbital radius of Sc^+ is ~ 1.8 Å dropping to ~ 1.3 Å for Cu^+ .¹³¹ Compare these radii to those for Li^+ , Na^+ , and Mg^+ , 0.70, 0.98, and 0.82 Å, respectively. This is shown visually in Figure 4, which shows M^+-NH_3 BDEs versus the inverse of the 3d orbital radii of the transition metal cations (TM^+) along with the inverse radii of the three alkali metal cations and Mg^+ . The

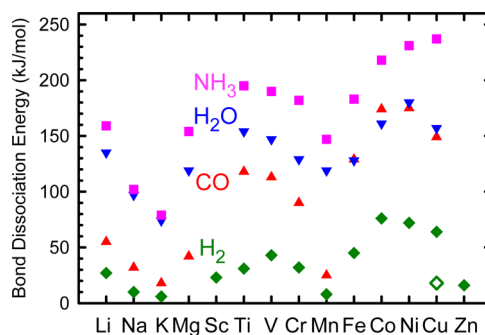


Figure 3. Bond dissociation energies of various metal cations to H_2 (green diamonds), CO (red triangles), H_2O (blue inverted triangles), and NH_3 (pink squares). The open symbol for $\text{Cu}^+(\text{H}_2)$ corresponds to the excited $^2\text{D}(4s^1 3d^9)$ state.

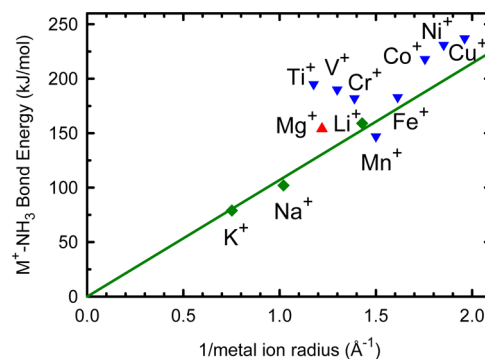


Figure 4. Bond dissociation energies of ammonia bound to alkali metal cations (green diamonds), magnesium (red triangle), and transition metal cations (blue inverted triangles) versus the inverse of the metal cation radius. The line shows a regression analysis of the data for the alkali metal cations constrained to pass through the origin.

line is a linear regression analysis of the alkali metal data constrained to pass through the origin. It can be seen that this line captures the overall trend in the data, but Mg^+ and most TM^+ lie higher than would be predicted by this line and Mn^+ lies below.

III.B.6.b. s - p and s - d Hybridization. The reason that Mg^+ lies above the line predicted from the alkalis is hybridization of the valence $3s$ electron. By mixing in $3p$ character, this electron can polarize away from the ligand. Although the hybridization costs energy, the ligand now can approach more closely to the cationic center, which also begins to have $2+$ character. A similar phenomenon occurs for TM^+ except now s - d hybridization (which requires less energy) is effective. This explains why most of the TM^+ also have BDEs lying above the line predicted by the alkali metals, but generally parallel this correlation.

III.B.6.c. Electronic State. The obvious exception to the previous conclusion is Mn^+ , but Fe^+ is also lower than its late metal counterparts (Co^+ – Cu^+). This can be explained by examining the ground electronic configuration of the atomic metal ions, $3d^n$ for Ti^+ – Cr^+ and Co^+ – Cu^+ , whereas Mn^+ and Fe^+ have $4s^1 3d^{n-1}$ ground state configurations. When NH_3 attaches to the $3d^n$ configuration, a strong dative bond is formed by donation of the nitrogen lone pair electrons into the empty $4s$ orbital. When the $4s$ orbital is occupied, the bond is much weaker because electron density is forced into an antibonding orbital and the ligand can no longer approach the metal center as closely.

This effect can also be seen in Figure 3, and is made more apparent in the data for the H_2 ligand. Here Mn^+ , Cu^+ (in its $1,3\text{D}$ states), and Zn^+ all have very low BDEs (Table 2). Each of these metal cations has a $4s^1 3d^{n-1}$ electronic configuration, consistent with such weak binding. For Fe^+ , the BDE to H_2 is substantially stronger than that to Mn^+ , an observation also true for the CO ligand. This indicates that Fe^+ promotes to its $3d^n$ excited configuration (which requires 24 kJ/mol) to bind these ligands. Such a promotion does not occur for Mn^+ with one ligand because its promotion energy is 113 kJ/mol.

III.B.6.d. π -Donor or Acceptor. Although the primary contribution to M^+ – L bonding is σ -donation from the ligand to the metal, the ability of the ligand to accept or donate electrons in π -orbitals is also influential and differs for early and late TMs. NH_3 cannot effectively donate or accept π -electrons, whereas CO and H_2 are both π -acceptors, and H_2O is a weak π -donor. The alkali cations and Mg^+ have no accessible π -electrons or empty π -orbitals and cannot utilize this to enhance bonding. Early TMs have half-occupied or empty π -orbitals and are therefore better π -acceptors, whereas late TMs have singly and doubly occupied π -orbitals and are more effective π -donors. These effects can be seen by comparing the average ratio of the BDEs to early and late TM^+ . For H_2 and CO , the late metals bind more strongly than the early metals by factors of 1.4–1.9, whereas for H_2O and NH_3 the ratios are 1.1–1.2, consistent with more effective π -backbonding for the late TMs. Nuances on these trends include the fact that Cr^+ ($3d^5$) has no empty orbitals to accept electron density, compared to Ti^+ and V^+ , which do.

III.B.6.e. Charge. Not surprisingly, the charge of the metal cation has an enormous effect on the binding energies. At this point in time, the only systematic BDEs available for multiply charged metal cations are those for hydration (Table 7). A comparison of the first hydration energies for the singly charged alkali metal cations along with Mg^+ to the doubly charged alkaline earth metal cations (which have closed shell rare-gas-like electronic configurations except for Mg^+) is shown in Figure 5 (along with a theoretical estimate of the Mg^{2+} – OH_2 bond energy¹⁶⁹ for completeness). As demonstrated above, both singly and doubly charged cations correlate with the

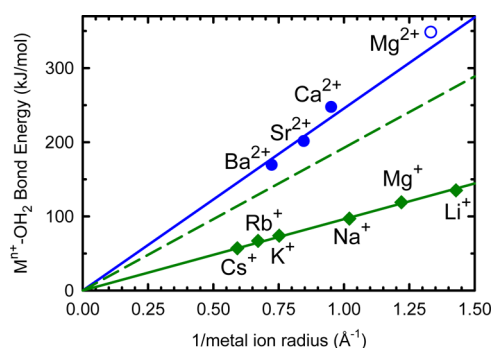


Figure 5. Bond dissociation energies of water bound to singly charged metal cations (green diamonds) and doubly charged alkaline earth metal cations (blue circles) versus the inverse metal cation radius. The open circle for Mg^{2+} indicates a theoretical value. Lines show regression analyses of each set of data constrained to pass through the origin. The green dashed line doubles the slope of the green solid line.

inverse of the metal cation radius raised to some power ($1/r$ shown). Clearly the metal dications have much stronger bonds than the monocations. When the slope of the monocation regression is doubled (dashed line), it can be seen that most of the increase is recovered, consistent with predominantly electrostatic binding.

III.B.7. Trends in Sequential BDEs. These various electronic effects also influence the magnitudes of the BDEs for additional ligands. For main group metal cations, sequential BDEs generally decline with increasing ligation, a consequence of increasing the electron density at the metal cation center and of enhanced ligand–ligand repulsion. This continues until the first solvent shell is completed. For transition metals, however, the electronic and hybridization effects lead to several interesting variations in this expected trend. As first noted by Squires¹⁰⁶ and Michl¹⁹² in their studies of the hydration of TM^+ , most TM^+ exhibit similar first and second ligand BDEs. This is primarily a consequence of s - d hybridization, which removes electron density along one axis such that two ligands on opposite sides of the metal center can benefit. Indeed, this effect can lead to the second BDE exceeding the first because the first ligand pays the cost of hybridization, which then benefits the second ligand. This effect is illustrated in Figure 6, which shows the sequential BDEs for Fe^+ bound to several ligands. In this case, the difference between the first and second ligands is enhanced because of the electronic effect associated with the sextet and quartet states of Fe^+ . Also shown here is the

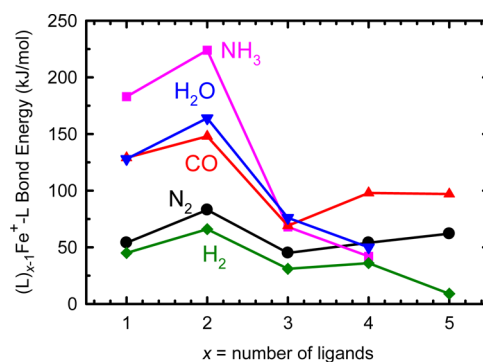


Figure 6. Sequential bond dissociation energies of iron cations to H_2 (green diamonds), N_2 (black circles), CO (red triangles), H_2O (blue inverted triangles), and NH_3 (pink squares).

Table 10. Sequential Bond Dissociation Energies (kJ/mol) of $M^+(L)_x$ Complexes for Miscellaneous Small Molecules^a

ligand	M^+	ref ^b	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
N ₂	Na ⁺	H ¹⁹⁴	33 (2)	22 (4)				
		Fe ⁺						
		C ⁸³	54 (6)	83 (9)	45 (6)	54 (4)	62 (4)	
		C ⁷⁹	53 (4)					
NO	Ni ⁺	E ^{195c}	56 (5)					
		C ¹²⁶	111 (11)	111 (11)	56 (4)	42 (10)		
		Li ⁺	60 (10)					
		C ¹⁹⁶	228 (8)	123 (7)	115 (5)			
		Cu ⁺	109 (5)	108 (6)				
CO ₂	Na ⁺	C ⁸⁰	67	46	41	35		
		H ¹⁹⁷	57 (4)					
		H ¹⁹⁴	58 (6)	48 (3)	44 (6)			
		C ⁸¹	62					
	Mg ⁺	P ¹⁹⁸	36					
		H ⁵	26 (4)					
		M ¹⁵⁶	74 (8)	122 (9)	37 (8)	90 (13)	69 (6)	
	Fe ⁺	C ¹⁹⁹	60 (4)					
		C ⁷⁹	54 (6)					
		E ^{195c}	49 (7)					
CS ₂	Mo ⁺	C ¹³⁶	114 (13)					
		T ¹⁴⁶	166 (5)	188 (6)				
	V ⁺	C ²⁰⁰	166 (10)					
		E ²⁰⁰	68 (13)					
CH ₄	Na ⁺	T ¹⁴⁶	30					
		H ¹²⁸	28 (7)	14 (7)				
	Mg ⁺	C ⁸¹	25 (1)	20 (1)	17 (1)	13 (2)	13 (2)	~12
		H ⁹¹	70 (3)	73 (2)	28 (6)			
	Ti ⁺	H ²⁰⁵	57 (3)	97 (4)	99 (6) ^d	74 (6) ^d		
		C ¹⁶¹	73 (2)	109 (2)	22 (1)	~21	~8	~8
	Fe ⁺	H ²⁰⁶	90 (6)	96 (5)	40 (5)	65 (6) ^e		
		C ⁸²	97 (2)	106 (2)	31 (1)	22 (1)	~8	~8
		H ²⁰³	96 (3)	104 (4)				
		H ²⁰⁴	104 (2)	111 (2)	39 (1)	~23	~8	~8
C ₂ H ₆	Ni ⁺	H ²⁰⁶	39 (2)					
		H ⁹¹	64 (6)					
	Al ⁺	C ²⁰²	117 (7)	112 (4)	<50			
		H ²⁰⁴	100 (5)					
	Co ⁺	C ²⁰¹						

^aUncertainties in parentheses. ^bC = threshold collision-induced dissociation, E = single temperature equilibrium, H = high-pressure temperature-dependent equilibrium, M = mobility, P = photodissociation, and T = threshold of endothermic reaction. ^cRelative free energy (E)¹⁹⁵ anchored to $D(\text{Fe}^+-\text{CH}_4)$ from ref 161. ^dThese bonds may correspond to $(\text{O}_2)\text{Fe}^+(\text{CH}_4)_{x-2}$. See discussion in ref 206. ^eMay be contaminated with $(\text{O}_2)\text{M}^+(\text{CH}_4)_2$. See discussion in ref 203.

observation that the third ligand is generally much weaker than the first two, also a consequence of s–d hybridization, which benefits two ligands but cannot easily accommodate more. For most ligands, the BDEs then decline (as for the alkalis) as more ligands are attached. For Fe⁺, it can be seen that both CO and N₂ do not follow this trend but rather show an increase. This is associated with an additional spin change in the complex as more ligands are attached. By lowering the spin (in this system, from the quartet to the doublet state associated with $\text{Fe}(\text{CO})_5^+$), electron density is removed from orbitals that can then more effectively accept electron density from the ligands. Another nice example of this effect is the increase in the BDE for $\text{V}^+(\text{H}_2)_6$ (Table 2), which is twice as large as that for $\text{V}^+(\text{H}_2)_5$, attributed to switching from a quartet state to a doublet.¹⁹³

III.B.8. Other Small Molecules. The sequential binding enthalpies for several additional small molecule ligands have also been measured. These ligands include N₂, NO, CO₂, CS₂, CH₄, and C₂H₆ and are included in Table 10. BDEs to N₂ have

been determined for Na⁺ ($x = 1$ and 2),¹⁹⁴ Fe⁺ ($x = 1-5$),^{79,83,195} and Ni⁺ ($x = 1-4$).¹²⁶ Isoelectronic with CO, the N₂ ligand binds more weakly to the transition metal cations by a factor of 0.6, whereas binding to Na⁺ is similar, probably because the ligands differ primarily in their π -acceptor capabilities. BDEs to NO have been measured for Li⁺ ($x = 1$),¹⁹⁶ Ni⁺ ($x = 1-3$),¹²⁶ and Cu⁺ ($x = 1$ and 2).⁸⁰ Because NO is a radical, it can bind as either a one or three electron donor. The very large Ni⁺–NO BDE is consistent with three electron donation, including covalent bond formation. BDEs to CO₂ have been measured for a wider array of metal cations: Na⁺ ($x = 1-4$),^{194,197} Mg⁺ ($x = 1-3$),^{81,198} Fe⁺ ($x = 1-5$),^{79,195,199} K⁺,⁵ Cs⁺,¹⁵⁶ and Mo⁺ ($x = 1$).¹³⁶ CS₂ has been measured for only transition metals: V⁺ and Mo⁺ ($x = 1$),¹⁴⁶ and Fe⁺ ($x = 1$ and 2).²⁰⁰ Both TCID (C)^{82,161,201,202} and high pressure temperature-dependent equilibria (H)^{91,128,203–206} have been used to measure BDEs for the simplest alkanes, CH₄ and C₂H₆, with several metal cations. Values for Fe⁺ and Co⁺ measured using both methods agree reasonably well and when they do not (as

Table 11. Bond Dissociation Energies (kJ/mol) of M⁺–L with Organic Ligands (O-Donors)^a

L	Li ⁺	Na ⁺	K ⁺	Mg ⁺	Al ⁺	Mn ⁺	Ag ⁺
CH ₃ OH	152 (10) ^b 151 (15) ^c 154 (8) ³⁴ 155 (9) ^{41,196}	92 (6) ²¹⁷ 97 (6) ¹⁰⁷ 110 (1) ²²¹ 99 (1) ¹¹⁵ 98 (3) ^d	92 (2) ²²⁴	146 (7) ⁸¹	138 (11) ^e 144 (11) ^f	126 (10) ^g	152 (8) ²³⁴ 138 (16) ¹⁶⁷ 148 (14) ²³⁵
C ₂ H ₅ OH	162 (10) ^b 164 (8) ³⁴ 164 (7) ^{41,196}	102 (4) ²¹⁷ 110 (6) ^{107,218} 106 (3) ^d		153 (7) ^h	153 (11) ^e 158 (11) ⁱ	132 (10) ^g	142 (15) ¹⁶⁷ 154 (17) ²³⁵
1-C ₃ H ₇ OH	169 (11) ^b 171 (8) ³⁴ 170 (9) ^{41,196}	108 (4) ²¹⁷ 114 (6) ²¹⁸ 113 (4) ²¹⁹ 109 (3) ^d	83 (4) ²²⁶	158 (7) ^h	159 (11) ^e 165 (11) ⁱ	137 (10) ^g	162 (19) ²³⁵
2-C ₃ H ₇ OH	170 (11) ^b 173 (8) ³⁴ 173 (8) ^{41,196}	113 (4) ²¹⁷ 117 (6) ²¹⁸ 123 ^k 113 (3) ^d		161 (7) ^h	163 (11) ^e 169 (11) ⁱ		156 (16) ²³⁵
1-C ₄ H ₉ OH	178 (8) ³⁴ 169 (8) ⁴¹ 177 (8) ^j 173 (11) ^l	109 (5) ²¹⁷ 116 (6) ²¹⁸ 110 (3) ^d		162 (7) ^h	163 (11) ^e 170 (11) ⁱ		164 (22) ²³⁵
<i>i</i> -C ₄ H ₉ OH	169 (8) ⁴¹ 172 (11) ^l	105 (6) ²¹⁷ 116 (6) ²¹⁸ 111 (3) ^d			163 (11) ^e 170 (11) ⁱ	141 (10) ^g	
2-C ₄ H ₉ OH	174 (9) ⁴¹ 175 (11) ^l	117 (5) ²¹⁷ 120 (6) ²¹⁸ 116 (3) ^d			167 (11) ^e 174 (11) ⁱ		
<i>t</i> -C ₄ H ₉ OH	178 (10) ⁴¹ 175 (11) ^l	117 (4) ²¹⁷ 121 (6) ²¹⁸ 117 (3) ^d			178 (11) ⁱ	148 (10) ^g	
CH ₃ OCH ₃	165 (11) ²¹² 158 (11) ^b 156 (15) ^c	92 (5) ²⁶⁰ 101 (6) ¹⁰⁷ 100 (3) ^d	73 (4) ²²⁵ 86 (4) ¹¹¹		158 (11) ^e 164 (11) ^f	133 (10) ^g	146 (8) ¹⁶⁶
C ₂ H ₅ OC ₂ H ₅	175 (11) ^l	117 (3) ^m 130 (1) ²²¹	93 (4) ¹¹¹	167 (7) ^h	180 (11) ⁱ	150 (10) ^g	139 (6) ¹⁶⁷
THF	173 (11) ^l			168 (7) ^h	177 (11) ^e 186 (11) ^f 114 (11) ^o 120 ^p	150 (10) ^g	
CH ₂ O	142 (11) ^l 143 (15) ⁿ				150 (11) ^e 153 (11) ^f	116 (10) ^g	
CH ₃ CHO	166 (11) ^b 170 (15) ⁿ	113 (3) ¹¹⁸		155 (7) ^h	150 (11) ^e 153 (11) ^f	134 (10) ^g	
CH ₃ COCH ₃	183 (11) ^b 183 (15) ⁿ	131 (4) ¹¹⁸ 139 (1) ²²¹ 128 (2) ¹¹⁵ 138 ^k	101 (10) ²⁰⁹ 108 (4) ²²³	173 (7) ^h	175 (11) ^e 181 (11) ^f	153 (10) ^g	<129 ²³⁸ 159 (6) ¹⁶⁷ 160 (19) ²³⁷
CH ₃ COC ₂ H ₅	190 (7) ¹⁹⁶ 191 (11) ^b	131 (7) ²¹⁹	95 (4) ²²⁶	177 (7) ^h	182 (11) ^e 190 (11) ⁱ	158 (10) ^g	
C ₂ H ₅ CO ₂ H	165 (6) ¹⁹⁶ 168 (11) ^b	118 (6) ²¹⁹	86 (4) ²²⁶				
HCO ₂ CH ₃	171 (15) ⁿ 171 (11) ^l				160 (11) ^e 165 (11) ⁱ	139 (10) ^g	
CH ₃ CO ₂ CH ₃	180 (15) ⁿ 183 (11) ^l	124 (3) ^m			182 (11) ^e 189 (11) ⁱ	154 (10) ^g	

^aValues are at 0 K (298 K values in italics) unless otherwise noted. Uncertainties are listed in parentheses. A = radiative association kinetics,²³⁷ C = threshold collision-induced dissociation,^{41,81,107,118,166,167,196,209,212,218,219,225,226,260} E = single temperature equilibrium,^{12,15,16,113,114,116,117,187–189,228} H = high-pressure temperature-dependent equilibrium,^{111,115,186,221,223} and P = photodissociation.²³⁸ ^bRelative free energy from ICR equilibrium (E) at 373 K^{12,13,113} Adjusted to 0 K using information from ref 196. ^cRelative free energy from ICR equilibrium (E) at 298 K¹¹⁴ Reanchored and adjusted to 0 K in ref 196. ^dRelative free energy from ICR equilibrium (E) at 298 K¹¹⁶ adjusted to 0 K using information in ref 217 or 107. ^eRelative free energy from ICR equilibrium (E) at 298 K¹⁸⁸ anchored as discussed in ref 186 and adjusted here from 298 to 0 K using information in ref 15 if possible. ^fRelative free energy from ICR equilibrium (E) at 298 K^{13,189} anchored here to *D*(Al⁺–CH₂O) from ref 186 and adjusted to 0 K using information calculated in ref 15 if possible. ^gAdjusted from relative free energies from ICR equilibrium (E) by symmetry number only.¹¹⁷ Anchored here to value for Mn⁺(C₆H₆) from Table 20. Values would be 11 kJ/mol higher if anchored to Mn⁺(NH₃) in Table 3. ^hRelative free energy from

Table 11. continued

ICR equilibrium (E),²²⁸ anchored and adjusted to 0 K in ref 81. ⁱRelative free energy (E)¹⁸⁹ anchored here to $D(\text{Al}^+-\text{CH}_2\text{O})$ from ref 186 and approximately adjusted to 0 K by adding $H_0 - G_{298} = 28 \pm 3$ kJ/mol, determined from average of calculated corrections in ref 15. ^jFrom ref 41 (C). Reevaluated in ref 34. ^kFeng and Gronert (K), unpublished as reported in ref 118. ^lRelative free energy from ICR equilibrium (E) at 373 K.^{12,16,113} Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^mRelative free energy from ICR equilibrium (E) at 298 K,¹¹⁶ adjusted to 298 K enthalpies using information in ref 115. ⁿRelative free energy from ICR equilibrium (E) at 298 K.¹⁸⁷ Reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. ^oHigh-pressure temperature-dependent equilibrium (H),¹⁸⁶ adjusted here from 298 to 0 K using information in ref 15. ^pTheoretical G4 value used in ref 15 to anchor their Al^+ scale.

noted in the Table 10 footnotes), it can be attributed to an O_2 contaminant in the TCID measurements, as explicitly studied in the equilibrium study for Co^+ .²⁰³ Not included in this table are values for mixed CO_2 and H_2O ligands on Na^+ ,¹⁹⁷ mixed H_2 , CH_4 , C_2H_6 , and H_2O ligands on Co^+ ,²⁰⁴ H_2 and CH_4 bound to CoCp^+ (where Cp = cyclopentadienyl),²⁰⁷ and NO bound to NiCp^+ .^{16,208}

III.C. Organic Ligands (O- and N-Donors)

III.C.1. Single Ligands. Table 11 lists the BDEs between metal cations and many oxygen containing organic ligands (alcohols, ethers, aldehydes, ketones, acids, and esters). Table 12 extends these results to nitrogen containing organic ligands (amines, nitriles, amides, and five- and six-membered heterocycles). Tables 11 and 12 are restricted to those ligands for which values are available for at least two metals. In many cases, the values have been reanchored here or adjusted to 0 K as detailed in the following. It should be noted that many more values are available for other ligands, in particular, for Li^+ and Na^+ .^{13,16,116,209} In addition, the kinetic method (K) has been used to determine the cesium cation affinities of many carboxylates (anchored there to an absolute scale)²¹⁰ and the relative affinities of many nitriles with Co^+ and Ni^+ .²¹¹ Single temperature ICR equilibria (E) have also been used to measure the relative free energies for many of these ligands with CpNi^+ .²⁰⁸

III.C.1.a. Lithium. By far and away, the most thermodynamic values for lithium cation affinities come from measurements of the relative affinities at a single temperature (E) using ICR mass spectrometry. Thus, these require an absolute anchor, which has been provided by TCID measurements,^{34,41,196,212} which has also contributed several absolute numbers for nitrogen heterocycles.^{28,213–216} These numbers have also been critically evaluated with respect to theory.^{12,196} Many of the relative lithium affinities in Tables 11 and 12 originate with a scale determined by Taft and co-workers using ICR equilibria at 373 K,¹⁰² which have been reevaluated subsequently by Burk et al.¹² Mayeux et al. recently revisited lithium basicity values above ~ 150 kJ/mol (~ 185 kJ/mol in affinity),¹³ anchoring this relative scale to the TCID value for pyridine.^{12,215} In several cases, these values can be adjusted to 0 K using theoretical enthalpy and entropy changes calculated elsewhere.¹⁹⁶ This latter reference also reanchored and adjusted to 0 K values from the 298 K ICR equilibrium study (E) of Woodin and Beauchamp.¹¹⁴ Other values from the 373 K ICR equilibria^{12,13,16,113} have been approximately adjusted to 0 K here by uniformly adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from a comparison of 0 K enthalpies¹⁹⁶ and 373 K free energies.^{12,113} This adjustment is also consistent with the average value for $T\Delta S_{373} = H_{373} - G_{373} = 36.1 \pm 3.4$ kJ/mol calculated by Mayeux et al.¹³ In addition, 298 K free energies from an ICR study (E) of Staley and Beauchamp¹⁸⁷ are anchored here and corrected approximately to 0 K using $H_0 - G_{298} = 26 \pm 2$ kJ/mol, the average correction calculated

elsewhere.¹⁹⁶ In cases where lithium ion affinities from Taft et al. have been supplanted by those measured more recently by Mayeux et al.,¹³ the former values are not tabulated.

III.C.1.b. Sodium. Absolute sodium cation affinities have been studied extensively using TCID methods (C)^{28,107,108,118,190,213–220} along with two high pressure temperature-dependent equilibrium studies (H) from the Castleman²²¹ and McMahon¹¹⁵ laboratories, Tables 11 and 12. As mentioned above, the sodium cation affinities from Castleman and co-workers tend to be systematically high: here 11, 11, 24, and 13 kJ/mol above the values from McMahon for methanol, acetone, methylamine, and diethyl ether, respectively; and 13,¹⁰⁷ 8,¹¹⁸ and 19¹⁰⁸ kJ/mol above the TCID values for the first three ligands (where the value for methanol from the competitive CID study¹⁰⁷ is believed to be more reliable than the direct TCID value²¹⁷). Additional values in Tables 11 and 12 come from 298 K equilibrium measurements (E) in an ICR,¹¹⁶ which were anchored to the high pressure temperature-dependent equilibrium value for $\text{Na}^+-\text{CH}_3\text{NH}_2$.¹¹⁵ These values have been adjusted here to 0 K when possible using information calculated elsewhere.^{107,217} When such corrections were unavailable, the free energies were adjusted here to 298 K enthalpies using information from another source.¹¹⁵

Additional values are also available from the kinetic method (K).²²² Here theory was used to establish an effective temperature of 994 K for six amides, and we have anchored these results here to the 0 K TCID value for $\text{Na}^+-\text{HCON}(\text{CH}_3)_2$.¹¹⁸ These values agree well with theoretical values obtained in this study, which were then used to obtain additional sodium cation affinities for imidazole, methylimidazole, and pyridazine (as well as dimethoxyethane).²²²

III.C.1.c. Potassium. BDEs for K^+ listed in Tables 11 and 12 are available from both high pressure temperature-dependent equilibrium (H)^{111,185,223,224} and TCID studies (C).^{28,209,213–216,225–227} Overlapping values from these two methods occur for dimethyl ether, acetone, 1-propylamine, dimethylformamide, and dimethylacetamide. The equilibrium values are systematically higher by 9 ± 3 kJ/mol, similar to the combined experimental uncertainties for the most precisely measured values. Dimethyl ether has the largest discrepancy of 14 ± 6 kJ/mol, and a theoretical value (78 kJ/mol)²²⁵ falls in between the two experimental values. Additional relative values are also available from the kinetic method (K).²²² Here comparison with theoretical values was used to establish an effective temperature of 843 K for six amides, and we have anchored these results here to the 0 K TCID value for $\text{K}^+-\text{HCON}(\text{CH}_3)_2$,²⁰⁹ after adjusting to 0 K using theoretical information.²²² These values agree well with theoretical values obtained in this study, which were then used to obtain additional potassium affinities for imidazole, methylimidazole, and pyridazine (as well as dimethoxyethane).²²²

III.C.1.d. Magnesium. Freiser and co-workers measured a series of relative magnesium cation affinities using single

Table 12. Bond Dissociation Energies (kJ/mol) of $M^+ - L$ with Organic Ligands (N-Donors)^a

L		Li ⁺	Na ⁺	K ⁺	Al ⁺	Mn ⁺	Ag ⁺
CH ₃ NH ₂		166 (10) ^b	132 ²²¹	80 (4) ¹¹¹			174 (10) ¹⁰⁸
	E, H	165 (15) ^c	108 (1) ¹¹⁵				
	E, C	167 (11) ^d	113 (6) ¹⁰⁸				
HN(CH ₃) ₂	E, H	167 (15) ^e	111 (8) ^f	82 (4) ¹¹¹			
	E	170 (11) ^d					
N(CH ₃) ₃	E, H	166 (15) ^e	109 (8) ^f	84 (4) ¹¹¹		154 (10) ^g	
	E	170 (11) ^d					
C ₂ H ₅ NH ₂	C		116 (10) ¹⁰⁸				179 (6) ¹⁰⁸
	E		116 (6) ^f				
1-C ₃ H ₇ NH ₂	C	198 (6) ¹⁹⁶	121 (6) ²¹⁹	79 (4) ²²⁶			
	H			89 (4) ¹¹¹			
HOC ₂ H ₄ NH ₂	C	290 (9) ¹⁹⁶	175 (7) ²¹⁹	126 (4) ²²⁶			
HCN	E	145 (15) ^e			117 (25) ^h	117 (10) ^g	
CH ₃ CN		177 (15) ^e	126 (10) ¹⁰⁸	102 (2) ¹⁸⁵	151 (11) ^j		171 (9) ¹⁰⁸
	E	178 (11) ^d	124 (6) ⁱ		157 (11) ^k	146 (10) ^g	
	E, C	175 (11) ^l	128 (5) ¹⁹⁰				162 (6) ²³⁶
C ₆ H ₅ CN	E, C	188 (11) ^d	137 (6) ¹⁰⁸		170 (11) ^j		174 (12) ¹⁰⁸
	C				180 (11) ^k		
HCONH ₂		193 (11) ^d	141 (4) ^m	111 (13) ^m			164 (17) ²³⁵
HCONH(CH ₃)		211 (15) ^l	150 (4) ^m	116 (13) ^m			170 (18) ²³⁵
HCON(CH ₃) ₂	E, C	222 (11) ^b	157 (4) ¹¹⁸	123 (13) ²⁰⁹	234 (11) ^k		184 (22) ²³⁵
	E, H		152 (3) ⁿ	129 (13) ²²³			
	K		150 ^o		234 (11) ^o		
CH ₃ CONH ₂	E, C	202 (11) ^d	144 (13) ²⁰⁹	125 (13) ²⁰⁹			176 (14) ²³⁵
	K		149 (4) ^m	117 (13) ^m			
CH ₃ CONHCH ₃	E, C	209 (11) ^d	149 (13) ²⁰⁹	129 (13) ²⁰⁹			187 (18) ²³⁵
	K		157 (4) ^m	123 (13) ^m			
CH ₃ CON(CH ₃) ₂	E, C	231 (11) ^l	158 (13) ²⁰⁹	124 (13) ²⁰⁹			200 (31) ²³⁵
	K		164 (4) ^m	128 (13) ^m			
	H			130 (8) ²²³			
pyrazole	C	187 (16) ²¹³	128 (9) ²¹³	84 (3) ²¹³			
	E, C	176 (11) ^d		80 (4) ²²⁷			
1-CH ₃ -pyrazole	C	207 (18) ²¹³	132 (3) ²¹³	94 (4) ²¹³			
	E	179 (11) ^d					
imidazole	C	211 (10) ²¹⁴	140 (5) ²¹⁴	109 (6) ²¹⁴	232 (8) ²²⁰	214 (4) ²²⁰	
	E, C	195 (10) ^b	139 (6) ²²⁰				
	K		146 (9) ^p	111 (9) ^p			
1-CH ₃ -imidazole	C	242 (20) ²¹³	161 (5) ²¹³	117 (3) ²¹³			
	E, K	216 (11) ^l	155 (9) ^p	119 (9) ^p			
1H-1,2,3-triazole	E	170 (11) ^d					
2H-1,2,3-triazole	C	136 (7) ²¹⁴	96 (4) ²¹⁴	55 (6) ²¹⁴			
1H-1,2,4-triazole	C	191 (8) ²¹⁴	124 (5) ²¹⁴	87 (5) ²¹⁴			
	E	172 (11) ^d					
2H-tetrazole	C	151 (7) ²¹⁴	115 (4) ²¹⁴	89 (5) ²¹⁴			
	E	175 (11) ^d					
pyridine	C	181 (15) ²¹⁵	127 (3) ²¹⁵	90 (4) ²¹⁵	190 (10) ²²⁹	182 (9) ²²⁹	
	E, H	182 (11) ^{b,l}		87 (4) ¹¹¹	193 (14) ^q		
	E	181 (15) ^e					
2-NH ₂ -pyridine	C	238 (21) ²¹⁶	146 (6) ²¹⁶	104 (4) ²¹⁶			
3-NH ₂ -pyridine	C	202 (10) ²¹⁶	136 (4) ²¹⁶	101 (3) ²¹⁶			
4-NH ₂ -pyridine	C	217 (20) ²¹⁶	147 (5) ²¹⁶	109 (3) ²¹⁶			
2-CH ₃ -pyridine	C	194 (7) ²⁸	128 (5) ²⁸	98 (3) ²⁸			
3-CH ₃ -pyridine	C	197 (15) ²⁸	133 (4) ²⁸	100 (3) ²⁸			
	E	188 (11) ^d					
4-CH ₃ -pyridine	C	196 (13) ²⁸	134 (4) ²⁸	99 (4) ²⁸			
pyridazine	C	234 (11) ²¹⁵	159 (3) ²¹⁵	130 (3) ²¹⁵			
	E, K	219 (11) ^l	159 (9) ^p	128 (9) ^p			
pyrimidine	C	154 (11) ²¹⁵	103 (4) ²¹⁵	69 (4) ²¹⁵	159 (6) ²³⁰	159 (10) ²³⁰	
	E	160 (11) ^d					
pyrazine	C	149 (13) ²¹⁵	107 (4) ²¹⁵	67 (4) ²¹⁵			
	E	155 (11) ^d					

Table 12. continued

L	Li ⁺	Na ⁺	K ⁺	Al ⁺	Mn ⁺	Ag ⁺
s-triazine	C	127 (13) ²¹⁵	88 (3) ²¹⁵	55 (3) ²¹⁵		

^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. C = threshold collision-induced dissociation,^{28,108,118,209,213–216,220,227,229,230} E = single temperature equilibrium,^{12,16,113,114,116,187–189,232} H = high-pressure temperature-dependent equilibrium,^{111,115,221,223} and K = kinetic method.²²² ^bRelative free energy (E) from ICR equilibrium at 373 K.^{12,13,113} Adjusted to 0 K using information from ref 196. ^cRelative free energy from ICR equilibrium (E) at 298 K.¹¹⁴ Reanchored and adjusted to 0 K in ref 196. ^dRelative free energy from ICR equilibrium (E) at 373 K.^{12,16,113} Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^eRelative free energy from ICR equilibrium (E) at 298 K.¹⁸⁷ Reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. ^fRelative free energy from ICR equilibrium (E) at 298 K¹¹⁶ and adjusted to 298 K ΔH using ΔS values calculated in this reference. ^gAdjusted from relative free energies from ICR equilibrium (E) by symmetry number only in ref 117. Anchored to value for $Mn^+(C_6H_6)$ from Table 20. Values would be 11 kJ/mol higher if anchored to $Mn^+(NH_3)$, Table 3. ^hRelative free energy from ICR equilibrium (E) at 298 K with water,²³² and anchored to $Al^+(H_2O)$ from ref 39. ⁱRelative free energy from ICR equilibrium (E) at 298 K¹¹⁶ and adjusted to 0 K in ref 190. ^jRelative free energy (E)¹⁸⁸ anchored as discussed in ref 186 and adjusted here from 298 to 0 K using information in ref 15 if possible. ^kRelative free energy (E)¹⁸⁹ anchored here to $D(Al^+-CH_2O)$ from ref 186 and approximately adjusted to 0 K by adding $H_0 - G_{298} = 28 \pm 3$ kJ/mol, determined from average of calculated corrections ref 15. ^lRelative free energy from ICR equilibrium (E) at 373 K.¹³ Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^mRelative kinetic method results (K) using an effective temperature of 994 K (Na^+) or 843 K (K^+) determined by comparison with theory,²²² anchored here to TCID value for $Na^+-HCON(CH_3)_2$ from ref 118 or $K^+-HCON(CH_3)_2$ from ref 209 after adjusting the latter to 0 K using theoretical information.²²² ⁿRelative free energy from ICR equilibrium (E) at 298 K¹¹⁶ and adjusted to 0 K using information in ref 118. ^oFeng and Gronert (K), unpublished work reported in ref 118. ^pRelative kinetic method results (K) anchored to theoretical values for five to six amides.²²² ^qRelative free energy (E)¹⁸⁹ anchored here to $D(Al^+-CH_2O)$ from ref 186 and adjusted here from 298 to 0 K using information in ref 15 if possible.

Table 13. Bond Dissociation Energies (kJ/mol) of M^+-L for First-Row Transition Metals with Organic Ligands (N-Donors) at 0 K^a

ligand	ref ^b	Sc ⁺	Ti ⁺	V ⁺	Cr ⁺	Mn ⁺	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺	Zn ⁺
imidazole	C ²²⁰	>182	>173	>216	220 (6)	214 (4)	246 (14)	269 (11)	284 (9)	288 (7)	252 (10)
pyridine	C ²²⁹	212 (10)	217 (9)	219 (14)	197 (11)	182 (9)	224 (9)	247(12)	255 (15)	246 (10)	247 (7)
	C								260 (8) ²⁴⁰	262 (8) ³	240 (4) ⁴
	K						204 (12) ²⁴¹	250 (21) ²⁴²	249 (16) ²⁴²	274 (75) ²⁵⁰	
pyrimidine	C ²³⁰	214 (9)	214 (10)	204 (7)	178 (6)	159 (10)	199 (8)	245 (14)	244 (9)	250 (10)	208 (7)
adenine	C ²³⁹		<354	<276	231 (8)	216 (7)	259 (9)	293 (11)	298 (10)	294 (11)	>233

^aUncertainties in parentheses. ^bC = threshold collision-induced dissociation,^{3,4,220,229,230,239,240} K = kinetic method,^{241,242} P = photodissociation.²⁵⁰

temperature equilibrium measurements (E) in an ICR.²²⁸ When one of these ligands (CH_3OH) was measured using TCID methods (C),⁸¹ these values were anchored and corrected to 0 K in that work, Table 11. Several absolute Mg^+ affinities at 0 K to nitrogen heterocycles obtained from TCID studies (C) include imidazole (244 ± 10 kJ/mol),²²⁰ pyridine (200 ± 6 kJ/mol),²²⁹ and pyrimidine (174 ± 6 kJ/mol).²³⁰

III.C.1.e. Aluminum. For Tables 11 and 12, the key measurement here is the absolute determination of the Al^+-CH_2O BDE (along with that for Al^+-CH_3F) using high pressure temperature-dependent equilibrium (H) studies by McMahon and co-workers.¹⁸⁶ McMahon and co-workers utilized their Al^+-CH_2O BDE to anchor relative aluminum cation affinities measured by single temperature equilibrium studies (E) in an ICR by Uppal and Staley.¹⁸⁸ This 298 K value has been adjusted to 0 K here using information calculated elsewhere.¹⁵ Additional relative free energies are available from studies by Gal et al.¹⁵⁸ as also reported more recently.¹³ In several cases, calculations performed in the latter reference provide detailed information that allows these values to be adjusted to 0 K after anchoring here to the experimental value for $D(Al^+-CH_2O)$.¹⁸⁶ In contrast, Gal, Yáñez, and Mó preferred to anchor their values to a $G4^{231}$ theoretical value for this molecule, also listed in Table 10. This raises the absolute BDEs by 6 kJ/mol. For other ligands, the correction to 0 K has not been explicitly determined. In these cases, the relative free energies from Gal et al.¹⁸⁹ are anchored here to

$D(Al^+-CH_2O)$ ¹⁸⁶ and approximately corrected to 0 K by adding $H_0 - G_{298} = 28 \pm 3$ kJ/mol. This correction is determined from the average of the calculated corrections of Gal, Yáñez, and Mó.¹⁵ The value for $D(Al^+-HCN)$ comes from measuring the equilibrium with water at a single temperature (E) using ICR,²³² and anchored to $D(Al^+-H_2O)$ from TCID work, Table 6.³⁹

III.C.1.f. Manganese. Most values for Mn^+ in Tables 11 and 12 originate from single temperature equilibrium measurements (E) by Uppal and Staley.¹¹⁷ The relative free energies measured here were approximately corrected to relative enthalpies considering only changes in the rotational symmetry number upon dissociation, which affects none of the values here except for the benzene ligand (where the correction is 1.7 kJ/mol). Here, we have anchored these values to the BDE for $Mn^+(C_6H_6)$ listed below in Table 20, 133 ± 9 kJ/mol.²³³ An alternative anchor would be $D(Mn^+-NH_3)$ from Table 3, in which case all values would be 11 kJ/mol higher. Table 12 also includes several absolute Mn^+ affinities to nitrogen heterocycles from TCID studies.^{220,229,230}

III.C.1.g. Silver. BDEs for Ag^+ in Tables 11 and 12 are largely threshold collision-induced dissociation measurements (C) from the laboratories of either Armentrout,^{166,234} Siu,^{108,167,235,236} or both for CH_3OH . For acetone, the TCID result is in good agreement with a value from radiative association kinetics (A),²³⁷ but well below an upper limit from photodissociation (P).²³⁸

Table 14. Sequential Bond Dissociation Energies (kJ/mol) of Bis-alcohol Complexes, $(R_1OH)M^+-R_2OH$ at 0 K^a

R ₁	M ⁺	ref ^b	R ₂								
			H	CH ₃	C ₂ H ₅	1-C ₃ H ₇	2-C ₃ H ₇	1-C ₄ H ₉	<i>i</i> -C ₄ H ₉	<i>s</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉
H	Li ⁺	C ³⁴	113 (10)	134 (5)	141 (5)	141 (7)					
	Na ⁺	C ¹⁰⁷	82 (6)	94 (6)	99 (7)						
CH ₃	Li ⁺	C ³⁴	111 (4)		131 (5)	130 (6)					
	Na ⁺	C ¹⁰⁷	83 (6)	86 (7)	99 (7)						
C ₂ H ₅	Li ⁺	C ³⁴	112 (5)	119 (5)		141 (7)	140 (7)	151 (9)			
	Na ⁺	C ²¹⁸	77 (7) ¹⁰⁷	86 (7) ¹⁰⁷		96 (5)	97 (5)	98 (5)	97 (5)	105 (5)	100 (4)
1-C ₃ H ₇	Li ⁺	C ³⁴	110 (6)	114 (6)	132 (7)			130 (12)			
	Na ⁺	C ²¹⁸			94 (5)			93 (5)	93 (7)		
2-C ₃ H ₇	Li ⁺	C ³⁴			131 (7)			124 (7)			
	Na ⁺	C ²¹⁸			91 (5)			94 (5)	89 (6)	95 (7)	96 (9)
1-C ₄ H ₉	Li ⁺	C ³⁴			35 (10)	124 (12)	122 (7)				
	Na ⁺	C ²¹⁸			93 (5)	90 (5)	94 (5)				
<i>i</i> -C ₄ H ₉	Na ⁺	C ²¹⁸			91 (5)	90 (5)	89 (6)				
<i>s</i> -C ₄ H ₉	Na ⁺	C ²¹⁸			95 (5)		92 (7)				
<i>t</i> -C ₄ H ₉	Na ⁺	C ²¹⁸			89 (4)		92 (9)				

^aUncertainties in parentheses. ^bReference for this row except as noted. C = threshold collision-induced dissociation.

III.C.1.h. Transition Metals. For the nitrogen heterocycles, imidazole, pyridine, pyrimidine, and adenine, Table 13 lists BDEs to the first-row transition metal cations measured primarily using TCID methods (C).^{3,4,220,229,230,239,240} These results also include a value for $D_0(\text{Ca}^+-\text{imidazole}) = 186 \pm 4$ kJ/mol. Values in reasonable agreement have been measured using the kinetic method (K) for pyridine bound to Fe^+ ,²⁴¹ Co^+ ,²⁴² and Ni^+ .²⁴² The latter reference also includes values for CpM^+ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$). A photodissociation (P) value for $\text{Cu}^+-\text{pyridine}$ agrees within its very large experimental uncertainty with the TCID results.

III.C.1.i. Trends. Comparison of BDEs for alcohols (ROH) and amines (RNH_2) shows that the metal cation affinity increases with the length of the alkyl chain, which can be attributed to increasing polarizability of the ligand (effects that can be quantified using additivity approaches²⁴³). Ethers and alcohols having the same number of carbons have similar metal cation BDEs, whereas secondary and tertiary amines have lower BDEs than the primary amine with the same number of carbons. Aldehydes, ketones, amides, and nitriles bind more tightly than the alcohols and amines, which can be attributed to a strong local dipole moment at the carbonyl or nitrile upon metal cation attachment. Electron delocalization reduces the bond strength for carboxylic acids and esters compared to ketones, whereas the amide carbonyl binds more tightly than the comparable ketone.

For the five-membered-ring nitrogen heterocycles, metal cation BDEs indicate a binding order of imidazole ($1,3\text{-C}_3\text{H}_4\text{N}_2$) > pyrazole ($1,2\text{-C}_3\text{H}_4\text{N}_2$) $\approx$ $1H\text{-}1,2,4\text{-triazole}$ ($\text{C}_2\text{H}_3\text{N}_3$) $\approx$ $1H\text{-}1,2,3\text{-triazole}$ ($\text{C}_2\text{H}_3\text{N}_3$) > $2H\text{-}1,2,3\text{-triazole}$ ($\text{C}_2\text{H}_3\text{N}_3$) > $2H\text{-}1,2,3\text{-triazole}$ ($\text{C}_2\text{H}_3\text{N}_3$). These trends can be explained by chelation of the metal ion when nitrogens having no hydrogen attached are adjacent and by electron delocalization from additional nitrogens. Methylation of imidazole and pyrazole enhances the BDEs. Electron delocalization effects are also seen in comparing the six-membered nitrogen heterocycles, where the BDEs fall in the order pyridine ($\text{C}_5\text{H}_5\text{N}$) > pyrimidine ($1,3\text{-C}_4\text{H}_4\text{N}_2$) > pyrazine ($1,4\text{-C}_4\text{H}_4\text{N}_2$) > $s\text{-triazine}$ ($1,3,5\text{-C}_3\text{H}_3\text{N}_3$). In contrast, pyridazine ($1,2\text{-C}_4\text{H}_4\text{N}_2$) enhances the binding compared to pyridine because the adjacent nitrogens can both bind to the metal cation. Methylation of pyridine enhances the BDEs slightly (primarily a polarizability

effect), whereas amination increases the BDEs significantly, with $2\text{-NH}_2\text{-pyridine}$ again able to chelate. Chelation also helps explain why adenine binds more tightly than pyridine and pyrimidine (Table 13), although adenine and imidazole have similar BDEs. This can be attributed to the larger dipole moment of the latter ligand (3.67 D versus 2.54 D).²²⁰

III.C.2. Sequential Ligation. For water and alcohol ligands, absolute BDEs for bis-ligated Li^+ and Na^+ have been measured using TCID methods (C) and are listed in Table 14.^{34,107,218} Also available (but not listed here) are TCID values for bis-ligated Na^+ complexes involving H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, NH_3 , C_6H_6 , and CH_3OCH_3 .¹⁰⁷ Relative values for up to four water and methanol ligands around all five alkali cations have been measured using single temperature equilibrium studies (E).²⁴⁴ These authors note that, although methanol binds more tightly than water in all systems, the enthalpic driving force decreases as the number of ligands increases and as the size of the metal cation increases. These differences were explained by noting that methanol has the larger polarizability, whereas water has the larger dipole moment.

Sequential ligation up to six O-donor and N-donor organic ligands (along with dimethyl sulfoxide) to metal cations have also been measured, with values listed in Table 15, except for molecules related to crown ethers (discussed below). A few single ligand systems are included here for completeness. TCID methods (C) are used to measure many of these values,^{81,83,209,234,240,245,246} with several systems for Cu^+ included.^{3,4,229,247,248} High pressure temperature-dependent equilibrium experiments (H) yield values for Na^+ , Al^+ , K^+ , and Ag^+ .^{112,186,221,223,249} Values obtained using the kinetic method (K) for several Fe^+ systems are included here for completeness,¹³³ along with an imprecise value for $\text{Cu}^+-\text{pyridine}$ obtained from photodissociation studies (P).²⁵⁰ BDEs for dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$, have been measured to Li^+ by ICR equilibrium (E) at 373 K and approximately adjusted to 0 K here,^{12,16,113} to Na^+ using ICR equilibrium (E) at 298 K and adjusted there to ΔH_{298} ,¹¹⁶ and to K^+ by an early TCID (C) measurement²⁰⁹ and high pressure temperature-dependent equilibrium (H).²²³ The values from the latter two experiments are within the combined experimental uncertainties. Trends in these values are comparable to those for the ligands discussed above. In addition, TCID methods have been used to measure

Table 15. Sequential Bond Dissociation Energies (kJ/mol) of $M^+(L)_x$ Complexes with Organic Ligands (O- and N-Donors)^a

ligand	M ⁺	ref ^b	x = 1	x = 2	x = 3	x = 4	x = 5	x = 6
CH ₂ O	Fe ⁺	C ⁸³	138 (7)	173 (8)	102 (5)	80 (6)		
		K ^{133c}	140 (11)					
CH ₃ OH	Na ⁺	H ²²¹	110 (1)	85 (1)	73 (2)	66 (1)		
	Mg ⁺	C ⁸¹	146 (7)	121 (7)	92 (9)			
	Co ⁺	C ²⁴⁵	148 (8)					
	Cu ⁺	C ²⁴⁶	178 (4)	187 (3)	73 (3)	66 (2)	50 (5)	30 (3)
	Ag ⁺	C ²³⁴	152 (8)	138 (7)	66 (6)	56 (8)		
	Cs ⁺	E ^{14d}	64					
CH ₃ CHO	Fe ⁺	K ^{133c}	149 (11)					
CH ₃ COCH ₃	Na ⁺	H ²²¹	140 (1)	105 (1)	87 (1)	62 (1)		
	K ⁺	H ²²³	109 (8)	88 (4)	67 (4)			
	Fe ⁺	K ^{133c}	173 (11)					
	Al ⁺	H ¹⁸⁶	175 (11) ^e	118 (4)				
	Cu ⁺	C ²⁴⁷	199 (4)	210 (7)	64 (3)	61 (5)		
HCON(CH ₃) ₂	K ⁺	H ²²³	130 (8)	88 (4)	63 (4)	54 (4)		
CH ₃ CON(CH ₃) ₂	K ⁺	H ²²³	130 (8)	100 (4)	75 (4)			
NH ₂ CH ₂ CH ₂ NH ₂	K ⁺	H ²⁴⁹	108 (2)	93 (2)	54 (1)			
(CH ₃) ₂ SO	Li ⁺	E ^f	225 (11)					
	Na ⁺	E ^{116g}	157 (3)					
	K ⁺	H ²²³	146 (13)	121 (8)	84 (4)	67 (4)	66 (4)	65 (4)
		C ²⁰⁹	129 (13)					
imidazole	Cu ⁺	C ²⁴⁸	288 (7)	258 (9)	80 (3)	64 (2)		
pyridine	Ni ⁺	C ²⁴⁰	260 (8)	251 (9)	142 (4)	87 (2)		
		C ²²⁹	255 (15)					
		K ²⁴²	249 (16)					
	Cu ⁺	C ³	262 (8)	236 (9)	82 (2)	60 (3)		
		C ²²⁹	246 (10)					
		P ²⁵⁰	274 (75)					
	Zn ⁺	C ⁴	240 (4)	155 (4)	102 (4)	76 (2)		
		C ²²⁹	247 (7)					
4,4'-dipyridyl	Ag ⁺	H ¹¹²			70 (1)	75 (1)		
	Ni ⁺	C ²⁴⁰	264 (5)	244 (11)	135 (6)	76 (4)		
	Cu ⁺	C ³	264 (11)	233 (7)	63 (2)			
	Zn ⁺	C ⁴	249 (9)	150 (7)	73 (4)			
2,2'-dipyridyl	Ni ⁺	C ²⁴⁰	≤408 (14)	271 (11)				
	Cu ⁺	C ³	370 (13)	238 (10)				
	Zn ⁺	C ⁴	349 (10)	225 (13)				
phenanthroline	Ni ⁺	C ²⁴⁰	≤415 (12)	272 (12)				
	Cu ⁺	C ³	395 (13)	233 (4)				
	Zn ⁺	C ⁴	395 (5)	237 (10)				

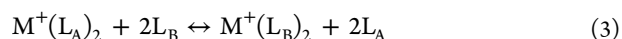
^aValues at 0 K with bond enthalpies at 298 K in italics. Uncertainties in parentheses. ^bC = threshold collision-induced dissociation, E = single temperature equilibrium, H = high-pressure temperature-dependent equilibrium, K = kinetic method, and P = photodissociation. ^cRelative kinetic method results (K)¹³³ anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ from ref 135. ^dRelative free energy (E) from ICR equilibrium, anchored in ref 14 to $D(\text{Cs}^+-\text{H}_2\text{O})$ from ref 152. ^eRelative free energy (E)¹⁸⁸ anchored as discussed in ref 186 and adjusted here from 298 to 0 K using information in ref 15. ^fRelative free energy from ICR equilibrium (E) at 373 K.¹³ Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^gRelative free energy from ICR equilibrium (E) at 298 K¹¹⁶ and adjusted to 298 K ΔH using ΔS values calculated in that reference.

the $(\text{Phen})_2\text{M}^{2+}$ –Phen BDE, where Phen = phenanthroline for M = Fe^{2+} (211 ± 11 kJ/mol), Co^{2+} (204 ± 12 kJ/mol), Ni^{2+} (213 ± 13 kJ/mol), Cu^{2+} (160 ± 10 kJ/mol), and Zn^{2+} (170 ± 14 kJ/mol).²⁵¹ Here the value for $\text{Fe}^{2+}(\text{Phen})_3$ is obtained assuming dissociation comes from an excited quintet state of the $\text{Fe}^{2+}(\text{Phen})_3$ complex. If the singlet ground state is assumed, the BDE is 236 ± 17 kJ/mol, which does not agree well with theory.

Trends in these data include the observation that the BDEs of pyridine and 4,4'-dipyridyl are similar to one another, whereas those for 2,2'-dipyridyl and Phen are much higher. The former two ligands are both monodentate, whereas the latter are bidentate. The rigid Phen ligand binds somewhat more

tightly than the more flexible 2,2'-dipyridyl, mainly because it has slightly higher polarizability and dipole moment.

For Co^+ ,²⁵² Cu^+ ,^{253,254} and Ag^+ ,²⁵⁵ single temperature equilibria (E) for exchange of two ligands (L_A and L_B) in reaction 3 could be established



such that relative free energies for the sum of the first two ligands could be measured. Selected values from these studies (which includes additional ligands) are included in Table 16 and compared to values measured using other methods, along with other available values for completeness.^{38,104,233} Cu^+ was studied by Staley²⁵³ and later by Kebarle,²⁵⁴ who adjusted the

Table 16. Bond Dissociation Energies (kJ/mol) for Loss of Both Ligands from $M^+(L)_2$ Complexes^a

M ⁺	L									
	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	C ₆ H ₆	(C ₂ H ₅) ₂ O	CH ₃ CO ₂ CH ₃	CH ₃ COCH ₃	NH ₃	CH ₃ CN	pyridine
Co ⁺	323 (9) ³⁸	360 (18) ^b	374 (18) ^b	423 (18) ²³³	399 (18) ^b		410 (18) ^b	467 (19) ¹⁰⁴		
Cu ⁺		369 (18) ^c	387 (18) ^c		418 (18) ^c	421 (18) ^c	416 (18) ^c	459 (18) ^c	472 (18) ^d	513 (18) ^d
	327 (11) ³⁸	365 (5) ²⁴⁶		373 (16) ²³³			409 (8) ²⁴⁷	483 (18) ¹⁰⁴	476 (10) ¹⁹¹	498 (12) ³
Ag ⁺	236 (13) ^e	270 (13) ^e	297 (13) ^e	285 (13) ^e	328 (13) ^e	307 (13) ^e	299 (13) ^e	358 (13) ^e	354 (13) ^e	
	247 (9) ¹¹²	290 (18) ²³⁴						329 (13) ^f		
	257 (11) ¹⁶⁶									

^aUncertainties in parentheses. C = threshold collision-induced dissociation,^{3,38,104,108,166,191,233,234,246,247} E = single temperature equilibrium,^{252–255} and H = high-pressure temperature-dependent equilibrium.¹¹² ^bRelative free energies from equilibria (E)²⁵² and anchored here as discussed in the text. ^cRelative free energies (E) at 298 K,²⁵³ adjusted to 298 K in ref 254, and anchored here as discussed in the text. ^dRelative free energies (E) at 393 K,²⁵⁴ anchored here as discussed in the text. ^eRelative free energies (E) at 393 K,²⁵⁵ adjusted to 298 K enthalpies using assumed entropy changes, and anchored to experimental ΔG_{298} for H₂O from ref 112. See text. ^fSum of the BDEs for $D(\text{Ag}^+ - \text{NH}_3)$ ¹⁰⁸ (adjusted to 298 K by adding 4 kJ/mol) and $D(\text{H}_3\text{N}^+ - \text{NH}_3)$,¹¹² Table 3.

Table 17. Sequential Bond Dissociation Energies (kJ/mol) of $M^+(L)_x$ Complexes for Crowns and Related Molecules^a

L	ref	x	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Al ⁺	Ag ⁺
CH ₃ OCH ₃	C	1	165 (11) ²¹²	92 (5) ²⁶⁰	73 (4) ²²⁵	59 (9) ²⁶¹	57 (5) ²⁶¹	158 (11) ^b	146 (8) ¹⁶⁶
	C	2	121 (6) ²¹²	82 (5) ²⁶⁰	69 (5) ²²⁵	55 (5) ²⁶¹	47 (6) ²⁶¹	95 (4) ¹⁸⁶	143 (8) ¹⁶⁶
	C	3	89 (8) ²¹²	69 (5) ²⁶⁰	57 (4) ²²⁵	37 (11) ²⁶¹	40 (9) ²⁶¹		65 (18) ¹⁶⁶
	C	4	68 (10) ²¹²	61 (4) ²⁶⁰	50 (8) ²²⁵				40 (10) ¹⁶⁶
C ₂ H ₅ OC ₂ H ₅		1	174 (11) ^c	117 (3) ^d	93 (4) ¹¹¹				139 (6) ¹⁶⁷
	H	2		96 (1) ²²¹				129 (4) ¹⁸⁶	
	H	3		69 (1) ²²¹					
(CH ₃ OCH ₂) ₂	C	1	241 (18) ²⁶²	158 (4) ²⁶⁰	119 (4) ²²⁵	92 (9) ²⁶¹	58 (5) ²⁶¹		
			244 (11) ^e	163 (3) ^f	127 (5) ²⁴⁹				
				166 (9) ^g	128 (9) ^g				
	K			195					
	H ¹²⁸			116 (8) ²⁶⁰	89 (12) ²²⁵	49 (12) ²⁶¹	54 (7) ²⁶¹		
12C4	C	1	372 (51) ^{262h}	252 (13) ²⁶⁰	189 (12) ²²⁵	93 (13) ²⁶¹ⁱ	85 (9) ²⁶¹ⁱ		
	C ²⁶³			244 (13)	182 (17)	152 (10)	137 (9)		
	A ²⁶⁹	2	135 (10)	144 (10)	135 (10)	128 (10)	110 (10)		
CH ₃ (OCH ₂ CH ₂) ₃ OCH ₃	A ²⁶⁹	2	108 (10)	127 (10)	128 (10)	123 (10)	102 (10)		
tetraaza-12C4	C ²⁶⁴	1		281 (12)	176 (8)	147 (5)	131 (6)		
15CS	C ²⁶⁵	1		294 (18)	205 (15)	114 (7) ⁱ	100 (6) ⁱ		
	C ²⁶⁶			296 (16)	216 (11)	175 (10)	159 (10)		
	A ²⁶⁹	2	104 (10)	118 (10)	138 (10)	133 (10)	125 (10)		
	C ²⁶⁵	1		296 (19)	234 (13)	191 (13)	168 (9)		
18C6	A ²⁶⁹	2	<94 (10)	<94 (10)	<94 (10)	<94 (10)	120 (10)		
diaza-18C6	C ²⁶⁷	1		296 (18)	239 (10)	192 (7)	161 (7)		
hexaaza-18C6	C ²⁶⁸	1		326 (13)	222 (9)	186 (8)	149 (6)		
dibenzo-18C6	R ²⁷⁰	1		295 (26)	221 (19)	183 (16) ^j	164 (14) ^j		

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. A = association, C = threshold collision-induced dissociation, E = single temperature equilibrium, H = high-pressure temperature-dependent equilibrium, K = kinetic method, and R = ion–molecule reaction bracketing. ^bRelative free energy from ICR equilibrium (E) at 298 K¹⁸⁸ anchored as discussed in ref 186 and adjusted here from 298 to 0 K using information in ref 15. ^cRelative free energy from ICR equilibrium (E) at 373 K.^{12,13,16,113} Adjusted to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^dRelative free energy from ICR equilibrium (E) at 298 K from ref 116 adjusted to 298 K enthalpies using information in ref 115. ^eRelative free energy from ICR equilibrium (E) at 373 K.¹³ Adjusted to 0 K using information in ref 196. ^fRelative free energy from ICR equilibrium (E) at 298 K from ref 116 adjusted to 0 K using information in ref 118. ^gRelative kinetic method results (K) anchored to theoretical values for five to six amides.²²² ^hReevaluated in ref 196. ⁱThese values correspond to excited conformations of these complexes. ^jThese values are obtained using the same procedure as ref 270 (average of 15CS and 18C6 values) using updated values for 15CS.¹⁹⁶

previous values to 298 K and anchored both scales to a theoretical value from Langhoff et al. for ammonia, 441 ± 18 kJ/mol,²⁵⁶ after adjusting from 0 to 298 K (addition of 8 kJ/mol). Anchored in this fashion, the $D(\text{Cu}^+ - 2\text{L})$ BDEs from the equilibrium measurements lie an average of 18 ± 15 kJ/mol below the five values taken from TCID measurements (L = NH₃,¹⁰⁴ CH₃CN,¹⁹¹ CH₃OH,²⁴⁶ acetone,²⁴⁷ and pyridine³).

Notably, a more advanced theoretical study by the same authors suggests the $D_{298}(\text{Cu}^+ - 2\text{NH}_3) = 456 \pm 18$ kJ/mol,²⁵⁷ and the experimental TCID value at 298 K is 491 ± 18 kJ/mol. Values shown in Table 16 have been anchored to minimize the average difference between these equilibrium values and those from TCID measurements.

For Co^+ , there is no overlap between the ligands studied by Jones and Staley²⁵² and absolute values obtained using other techniques.^{38,104,233} Comparison of the Co^+ –2L and Cu^+ –2L BDEs for L = NH_3 , H_2O , and C_2H_4 in Tables 3, 6, and 19, respectively, suggest that the former are $97 \pm 2\%$ of the latter. The values listed in Table 16 use this approximation while retaining the differences in relative free energies measured via equilibrium.

For Ag^+ , Deng and Kebarle anchored their relative free energy scale (E) measured at 393 K to the absolute value for $\Delta G_{298}(\text{Ag}^+ - 2\text{H}_2\text{O})$ measured using high pressure temperature-dependent equilibrium (H)¹¹² after correcting for the temperature difference. Enthalpies at 298 K were obtained by using estimated entropy changes. Notably the entropies estimated in these two works differ leading to an enthalpy sum that differs by 9 kJ/mol. Thus, these values for H_2O and CH_3OH are somewhat low compared to TCID results (C) by similar amounts,^{166,234} whereas the value for NH_3 is high compared with a value that combines the first and second BDEs from different sources.^{108,112}

III.C.3. Crown Ethers and Related Molecules. The interaction of alkali metal cations with oxygen crown ethers, $c\text{-(C}_2\text{H}_4\text{O)}_x$, is the poster child for host–guest interactions, which have been nicely reviewed elsewhere.^{17,258,259} Table 17 lists the relevant gas-phase work mainly for the five alkali metal cations but also including two additional metal cations for which sequential BDEs of ethers are available. Most of this thermodynamic information comes from systematic studies using TCID (C),^{166,212,225,260–268} but additional absolute values are available from high pressure temperature-dependent equilibria (H),^{111,128,186,221} along with relative values anchored as described from single temperature equilibria (E)^{13,116,128,188} and kinetic method (K)²²² studies. Notably, the value for Li^+ (dimethoxyethane) is among the values revisited by Mayeux et al.,¹³ and lies 21 kJ/mol higher than the previous value derived from Taft et al. (not included in Table 17),^{12,16,113} making it agree nicely with the TCID value.²⁶² BDEs for the second 15-crown-5 (15C5, $c\text{-(C}_2\text{H}_4\text{O)}_5$) and 18-crown-6 (18C6, $c\text{-(C}_2\text{H}_4\text{O)}_6$) ligands to all five alkali cations have been determined using radiative association kinetics (A)²⁶⁹ and ion–molecule reaction bracketing (R) has determined that the BDEs of dibenzo-18C6 to the alkali cations lie between the respective values for 15C5 and 18C6.²⁷⁰ Additional values for Li^+ and Na^+ bound to dimethyl ether and diethyl ether can be found in Table 11, but are not included here so that trends in the data can be highlighted.

In the initial TCID measurements of the BDEs of 12C4 and 15C5 to Rb^+ and Cs^+ ,^{261,265} comparison with theory suggested that these values probably corresponded to excited conformers of these complexes, hypothesizing that they were kinetically trapped. More recent TCID measurements confirm this by generating the complexes using a different ion source, obtaining BDEs that agree much better with theory, which also permits the excited conformers to be identified.^{263,266} Notably, this reassignment also affects the values reported for dibenzo-18C6 for Rb^+ and Cs^+ ,²⁷⁰ and these values have been revised here using the updated 15C5 BDEs for Rb^+ and Cs^+ .

III.C.3.a. Chelation. One of the key features associated with these data is the effect of chelation on the BDEs. This is illustrated in Figure 7 for potassium cations and shows the sum of the BDEs for one to four dimethyl ether (DME) ligands, one and two dimethoxyethane (DXE) ligands, the oxygen crowns (12C4, 15C5, and 18C6), and nitrogen crowns (cyclen =

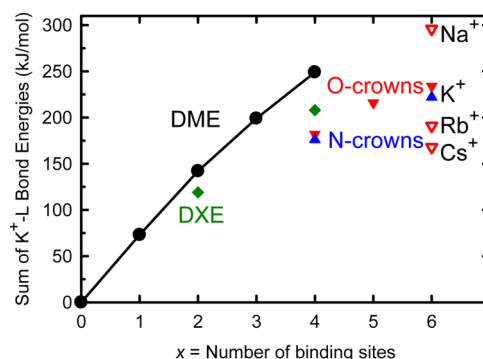


Figure 7. Sum of the bond dissociation energies of potassium cations to dimethyl ether (DME, black circles), dimethoxyethane (DXE, green diamonds), 12C4, 15C5, and 18C6 (O-crowns, red inverted triangles), and tetraaza-12C4 and hexaaza-18C6 (N-crowns, blue triangles) as a function of the number of binding sites in all ligands. Values for 18C6 bound to the other alkali metal cations are shown as open symbols.

tetraaza-12C4 and hexacyclen = hexaaza-18C6) as a function of the number of binding sites (O or N). As discussed above for other ligands, the sequential BDEs to DME gradually decline as the number of ligands increases, which can be seen in Figure 7 as the gradually decreasing slope of the DME line. DXE, which now has two oxygen sites, falls below the summed DME values by 23 and 41 kJ/mol at $x = 2$ and 4, respectively, such that the geometric constraint associated with the bidentate DXE ligand reduces its ability to bind as tightly as the unconstrained DME ligands. Likewise, 12C4, with four oxygen sites, binds less tightly than two DXE ligands by 26 kJ/mol. Larger O-crowns bind more tightly, increasing gradually with the number of oxygens but less rapidly than the DME trend. This is true for K^+ , Rb^+ , and Cs^+ , whereas for Na^+ the BDEs for 15C5 and 18C6 are the same within experimental uncertainty. This result can be attributed to the small size of Na^+ , which does not allow efficient coordination of all six oxygens in 18C6. Table 17 also shows that a second triglyme ligand, the acyclic version of 12C4, binds somewhat less strongly than the second crown. This result can be rationalized because the first acyclic ligand can more completely surround the metal cation than the constrained cyclic ligand, such that a second crown ligand binds more tightly to the exposed metal cation than a second acyclic ligand.

Comparing the nitrogen crowns to the oxygen crowns shows that substituting NH for O reduces the BDE slightly for K^+ , Rb^+ , and Cs^+ , whereas Na^+ exhibits the opposite trend. This is because harder metal cations prefer the more basic nitrogen donor atoms and thus Na^+ binds more strongly to cyclen and hexacyclen than 12C4 and 18C6, respectively, whereas this trend reverses as the size of the alkali metal cation increases and its hardness decreases.

III.C.3.b. Periodic Trends. One particularly interesting aspect of these data is the periodic trends. As for other ligands, all the BDEs increase in strength as the metal cation gets smaller (with the exception of the second 12C4 and triglyme ligands). In the gas phase, this result is expected for reasons elucidated above, but nevertheless is somewhat surprising in the present context because, in solution, 18C6 is known to bind to K^+ selectively. This has commonly been attributed to the fact that the size of the potassium cation is nearly equal to the size of the cavity created by a planar array of the six oxygen atoms in 18C6. What the gas-phase data demonstrates is that this selectivity is actually a balance between the effects of solvation of the metal

Table 18. Bond Dissociation Energies (kJ/mol) of $M^+(\text{Ligand})$ Complexes Involving Ligands Employed as MALDI Matrices at 0 K^a

ligand	Na ⁺		K ⁺	
	TCID	kinetics ^{274b}	TCID ²⁷³	kinetics ²⁷⁵
benzoic acid	130 (4) ²⁷¹		92 (3)	
2-OH-benzoic acid	143 (4) ²⁷¹		102 (3)	
3-OH-benzoic acid	131 (3) ²⁷¹		99 (4)	
4-OH-benzoic acid	132 (5) ²⁷¹		103 (3)	
2,3-(OH) ₂ -benzoic acid	145 (4) ²⁷¹		98 (4)	
2,4-(OH) ₂ -benzoic acid	145 (4) ²⁷¹		108 (3)	
2,5-(OH) ₂ -benzoic acid	145 (5) ²⁷¹	148 (5) ^c	102 (2)	126 (4) ^d
2,6-(OH) ₂ -benzoic acid	145 (4) ²⁷¹		96 (2)	
3,4-(OH) ₂ -benzoic acid	138 (3) ²⁷¹		104 (8)	
3,5-(OH) ₂ -benzoic acid	136 (7) ²⁷¹		99 (3)	
nicotinic acid	125 (3) ²⁷²	155 (4) ^c		
quinoline	143 (4) ²⁷²			
3-aminoquinoline	147 (5) ²⁷²	133 (5) ^c		
4-nitroaniline	162 (5) ²⁷²	144 (5) ^c		
picolinic acid	174 (5) ²⁷²			
3-OH-picolinic acid	171 (6) ²⁷²	155 (4) ^c		
4-OH- α -cyanocinnamic acid		154 (5) ^e		
6-aza-2-thiothymine		150 (5) ^e		
ferulic acid		149 (4) ^e		
sinapinic acid		148 (4) ^e		131 (4) ^d
2,4,6-(OH) ₃ -acetophenone		143 (4) ^e		124 (4) ^d
dithranol		140 (3) ^e		121 (3) ^d

^aUncertainties in parentheses. ^bAn additional correction of -37 kJ/mol has been applied here to reanchor the free energy values to $D(\text{Na}^+ - \text{DXE})$ from ref 260 rather than from ref 128; see Table 17 and text. ^cRelative free energy values determined from reaction kinetics in ref 274 and adjusted to 0 K using computed thermal corrections determined in ref 271 or 272. ^dRelative free energy values determined from reaction kinetics in ref 275 and adjusted to 0 K using the computed thermal correction (27 kJ/mol) determined in ref 273 for 2,5-(OH)₂-benzoic acid. ^eRelative free energy values determined from reaction kinetics in ref 274 and adjusted to 0 K using the average computed thermal corrections (26 ± 2 kJ/mol) determined in refs 271 and 272.

cations and their complexation with the crown ether ligand. When the hydration enthalpies and crown ether complexation energies are compared, the solution phase selectivity for the potassium cation is recovered.²⁵⁹ Further implications and analysis of these trends can be found elsewhere.¹⁷

III.C.4. MALDI Matrix Molecules. Table 18 lists the sodium and potassium cation ion affinities of 22 molecules used as matrices in matrix assisted laser desorption ionization (MALDI), various benzoic acids, and other aromatic heterocycles. Many of these values come from TCID studies (C) in the Rodgers laboratory for both sodium^{271,272} and potassium.²⁷³ The remaining values were determined by Zenobi and co-workers using ligand displacement reactions with dimethoxyethane (DXE) and explicit analysis of the time dependent kinetics.^{274,275} An equilibrium approach yielded similar relative energies, but the kinetic analysis was preferred in all cases except 4-nitroaniline where the kinetic approach failed because formation of $\text{Na}^+(\text{4-nitroaniline})_2$ complicated the analysis. Notably, these authors anchored their relative free energy scale for sodium to the $\text{Na}^+(\text{DXE})$ value reported by Castleman and co-workers,¹²⁸ which seems too high for reasons discussed above. If these values are reanchored to the TCID value for $\text{Na}^+(\text{DXE})$,²⁶⁰ Table 17, the values are lowered by 37 kJ/mol. For several of the matrix molecules, explicit corrections from 298 K free energies to 0 K enthalpies are available and yield an average correction of 26 ± 2 kJ/mol, which is then applied in Table 18 to the remaining values as well. Although the agreement between the sodium cation affinities obtained by TCID and the kinetic approach for 2,5-(OH)₂-benzoic acid is

now good, agreement for the other four overlapping molecules remains poor; however, the 37 kJ/mol reanchoring suggested here lowers the mean absolute deviation between these sets of numbers from 34 ± 20 to 18 ± 11 kJ/mol. For the single case where both approaches were used for potassium affinities, the values also do not agree very well. These remaining discrepancies are not understood.

III.D. π -Ligands (Alkenes, Alkynes, Benzene, Substituted Benzenes)

III.D.1. Ethene. Table 19 lists BDEs for one and two ethene ligands to a variety of metal cations, including the entire first-row transition metal cations. The latter were measured using TCID techniques (C),^{135,201} which also provide the value for Na^+ ,¹¹⁸ whereas BDEs for Al^+ and Ag^+ were determined by high pressure temperature-dependent equilibrium studies (H).^{91,276} Uniquely, multiple methods have been used to determine $D(\text{Co}^+ - \text{C}_2\text{H}_4)$, with values from TCID and analysis of kinetic energy release distributions (D)⁴⁴ being in good agreement. Trends in these values parallel the discussion above for other ligands.

III.D.2. Benzene. Table 20 lists the first and second BDEs for benzene to many metal cations. In only one case, K^+ , have BDEs for additional ligands been measured: 55 and 53 kJ/mol for $x = 3$ and 4, respectively, at 298 K.²⁷⁷ For the first two ligands, several methods have been applied to many of the metal systems. For Li^+ and Na^+ , the values for a single ligand from TCID (C) measurements^{107,118,278} agree nicely with those taken from relative free energy values obtained from ICR equilibrium measurements (E),^{12,113,114} which lie well below

Table 19. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{C}_2\text{H}_4)_{x-1}\text{M}^+-\text{C}_2\text{H}_4^a$

M^+	ref ^b	$x = 1$	$x = 2$
Na^+	C ¹¹⁸	43 (4)	
Al^+	H ⁹¹	62 (3)	~38
Ti^+	C ¹³⁵	146 (11)	
V^+	C ¹³⁵	125 (8)	127 (14)
Cr^+	C ¹³⁵	96 (11)	108 (11)
Mn^+	C ¹³⁵	91 (12)	88 (14)
Fe^+	C ¹³⁵	145 (11)	151 (15)
Co^+	C ¹³⁵	186 (9), 179 (7), ^c 176 (21) ^d	152 (14)
Ni^+	C ¹³⁵	182 (11)	173 (14)
Cu^+	C ¹³⁵	176 (14)	174 (13)
Ag^+	H ²⁷⁶	141	136

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. ^bC = threshold collision-induced dissociation, D = kinetic energy release distribution, and H = high-pressure temperature-dependent equilibrium. ^cThreshold collision-induced dissociation (C) value from ref 201. ^dKinetic energy release distribution (D) analysis from ref 44.

the high pressure temperature-dependent equilibrium value (H) for $\text{Na}^+(\text{C}_6\text{H}_6)$ from Castleman and co-workers.²⁷⁹ In contrast, the values for K^+ binding one and two benzene ligands from TCID²⁷⁸ and high pressure temperature-dependent equilibria agree well.²⁷⁷ It should also be noted that there are three values listed for $\text{Na}^+(\text{C}_6\text{H}_6)$ taken from TCID work: the originally reported value of 88 ± 4 kJ/mol,¹¹⁸ a value of 93 ± 6

kJ/mol that incorporates a refined analysis,²⁷⁸ and a value of 95 ± 6 kJ/mol resulting from analysis of multiple competitive dissociations.¹⁰⁷ The latter two values are preferred and agree very well with the value from McMahon and co-workers of 93 ± 3 kJ/mol.¹¹⁶ For Mg^+ , the TCID value⁸¹ lies above the upper limit from photodissociation (P),²⁸⁰ plausibly because the ions were not as cold as believed in the latter study. The former value agrees better with theoretical values of 132 and 127 kJ/mol.^{81,281} For Al^+ , the only measurement comes from radiative association kinetics (A).²⁸²

For the transition metal cations where there is overlap, TCID values²³³ generally fall somewhat below values from photodissociation (P),^{280,283–286} but agree nicely with values from radiative association kinetics (A) for Cr^+ and Ag^+ .^{237,287} For $\text{Ti}^+(\text{C}_6\text{H}_6)$, the limit cited comes from observing exothermic dehydrogenation of cyclohexane.²⁸³ The values for $\text{Cr}^+(\text{C}_6\text{H}_6)$ and $\text{Cu}^+(\text{C}_6\text{H}_6)$ in this work are obtained by photodissociation thresholds for CrFe^+ and CuFe^+ coupled with the observation that benzene displaces Fe in these complexes. Freiser and co-workers also used a novel continuous ICR ejection technique to monitor the metastable formation of $\text{Cr}^+(\text{C}_6\text{H}_6)$ and $\text{Mn}^+(\text{C}_6\text{H}_6)$,²⁸⁸ finding values in good agreement with the TCID work, but this method has not seen general application. For the $(\text{C}_6\text{H}_6)\text{Ag}^+-\text{C}_6\text{H}_6$ BDE, the value in Table 20 is obtained by combining $D_0(\text{Ag}^+-\text{C}_6\text{H}_6) = 156 \pm 7$ kJ/mol²⁸⁹ with $D_{298}(\text{Ag}^+-2\text{C}_6\text{H}_6) = 285 \pm 13$ kJ/mol from Table 16. The plausibility of these values is suggested by noting that the second BDE to Ag^+ is $83 \pm 10\%$ of the first BDE, which is

Table 20. Sequential Bond Dissociation Energies (kJ/mol) of $(\text{C}_6\text{H}_6)_{x-1}\text{M}^+-\text{C}_6\text{H}_6^a$

M^+	ref ^b	$x = 1$	$x = 2$
Li^+	C ²⁷⁸	161 (14), 147 (10), ^c 150 (15) ^d	104 (7)
Na^+	C ²⁷⁸	93 (6), 95 (6), ¹⁰⁷ 88 (4), ¹¹⁸ 93 (5), ^e 112 (6) ^f	80 (6)
K^+	C ²⁷⁸	74 (4), 76 (6) ^g	68 (7), 71 (6) ^g
Rb^+	C ²⁷⁸	69 (4)	63 (8)
Cs^+	C ²⁷⁸	65 (5)	59 (8)
Mg^+	C ⁸¹	134 (10), <113 ²⁸⁰	
Al^+	A ²⁸²	147 (10) ^h	
Sc^+	P ²⁸⁶	209 (13)	209 (13)
Ti^+	C ²³³	259 (9), >204 ²⁸³	253 (18)
V^+	C ²³³	234 (10), 259 (21) ²⁸⁴	246 (18), 238 (21) ²⁸⁴
Cr^+	C ²³³	170 (10), 231 (38), ²⁸³ 169 (10), ²⁸⁸ 164 (14) ²⁸⁷	232 (18), 212 (39) ²⁸⁷
Mn^+	C ²³³	133 (9), 145 (10) ²⁸⁸	203 (16)
Fe^+	C ²³³	207 (12), 231 (21), ²⁸⁴ 202 (8), ⁱ <260 ²⁸⁰	187 (16)
Co^+	C ²³³	256 (11), 285 (21) ²⁸⁴	167 (14)
Ni^+	C ²³³	243 (11), 285 (21) ²⁸⁴	147 (12)
Cu^+	C ²³³	218 (10), 217 (6), ²⁹⁰ 209 (38), ²⁸³ <191 ²⁸⁰	155 (12)
Y^+	P ²⁸⁶	209 (13)	197 (13)
Nb^+	P ²⁸⁶	268 (13)	205 (13)
Ag^+	C ²⁸⁹	156 (7), 162 (19), ²³⁷ <126, ²⁸⁰ <230 (5) ²⁸⁵	129 (15) ^j
Cd^+	A ²³⁷	136 (19)	
La^+	P ²⁸⁶	209 (13)	<180
Bi^+	P ²⁸⁰	<149	

^aUncertainties in parentheses. ^bReference for this row except as noted. A = radiative association kinetics,^{237,287} C = threshold collision-induced dissociation,^{107,118,290} and P = photodissociation.^{280,283–285} ^cRelative free energy (E) from ICR equilibrium at 373 K.^{12,113} Adjusted to 0 K in ref 196. Additional $T\Delta S = RT \ln(2) = 2.1$ kJ/mol factor included here. ^dRelative free energy (E) from ICR equilibrium at 298 K.¹¹⁴ Reanchored and adjusted to 0 K in ref 196. Additional $T\Delta S = RT \ln(2) = 1.7$ kJ/mol factor included here. ^eFree energy from ICR equilibrium (E) at 298 K.¹¹⁶ Adjusted here to 0 K using information in ref 118 and an additional $T\Delta S = RT \ln(2) = 1.7$ kJ/mol factor. ^fHigh pressure temperature-dependent equilibrium (H) enthalpy.²⁷⁹ Adjusted to 0 K here using information in ref 118. ^gHigh pressure temperature-dependent equilibrium (H) enthalpies adjusted for unimolecular dissociation.²⁷⁷ Adjusted here to 0 K using information in ref 278. ^hConverted to 0 K in ref 15. ⁱRelative kinetic method value (K) from ref 133 anchored using $\text{Fe}^+(\text{C}_2\text{H}_4) = 144.3 \pm 10.6$ kJ/mol from ref 135. Additional $T\Delta S = RT \ln(2) = 1.7$ kJ/mol factor included here. ^jCalculated from the two ligand BDE in Table 6 and $D_0(\text{Ag}^+-\text{C}_6\text{H}_6)$ from ref 289.

Table 21. Sequential Bond Dissociation Energies (kJ/mol) of $M^+(L)_x$ Complexes for π -Ligands: Pyrroles, Substituted Benzenes, and Larger Aromatic Rings^a

π -ligand	ref ^b	x	M^+							
			Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ⁺	Al ⁺	Cu ⁺
pyrrole	C ²²⁷	1	177 (17)	101 (8)	79 (4)	71 (7)	50 (3)	157 (10) ^c	173 (8) ²⁹¹	239 (13) ²⁹⁰
	C ²¹³			102 (5)	84 (4)			184 (21) ²⁹¹	184 (21) ²⁹¹	247 (21) ²⁹¹
	C ²²⁷	2	110 (4)	87 (5)	70 (4)	67 (4)	48 (3)	<109 ²⁹¹	<105 ²⁹¹	184 (21) ²⁹¹
1-CH ₃ -pyrrole	C ²¹³	1	186 (17)	111 (4)	88 (6)					252 (10) ²⁹⁰
toluene	C ²⁹²	1	183 (16)	112 (4)	80 (5)	71 (4)	64 (4)			219 (10) ²⁹⁰
	E		158 (11) ^d							
	C ²⁹²	2	117 (3)	87 (2)	75 (5)	68 (4)	62 (4)			
aniline	C ²⁹⁴	1	192 (22)	120 (3)	83 (3)	76 (5)	70 (4)			248 (9) ²⁹⁰
	H ¹¹¹				95 (4)					
	C ²⁹⁴	2	128 (4)	99 (2)	76 (3)	72 (4)	66 (3)			
N-CH ₃ -aniline	C ²⁹⁵	1	197 (10)	125 (3)	97 (3)	85 (3)	76 (3)			234 (8) ²⁹⁰
N,N-(CH ₃) ₂ -aniline	C ²⁹⁵	2	122 (5)	102 (3)	73 (3)	68 (2)	64 (2)			
	C ²⁹⁵	1	210 (8)	129 (4)	99 (3)	92 (2)	83 (2)			233 (12) ²⁹⁰
	C ²⁹⁵	2	128 (4)	99 (2)	76 (3)	72 (3)	66 (3)			
phenol	C ²⁹⁶	1	179 (16)	102 (3)	74 (3)	69 (4)	65 (5)	160 (16) ²⁹⁷	159 (17) ²⁹⁷	
			162 (11) ^e	99 (3) ¹¹⁸						
				97 (8) ^f						
F-benzene	C ²⁹⁶	2	115 (3)	82 (3)	68 (3)	64 (4)	60 (4)			
	C ³⁰⁰	1	147 (20)	70 (3)	55 (3)	54 (5)	50 (5)			183 (5) ²⁹⁰
	C ³⁰⁰	2	95 (3)	66 (4)	50 (3)	47 (5)	45 (4)			
Cl-benzene	C ²⁹⁹	1	133 (11) ^d	74 (3)	56 (3)					195 (5) ²⁹⁰
Br-benzene				80 (8) ^f						
	C ²⁹⁹	1	135 (11) ^d	81 (3)	66 (3)					212 (8) ²⁹⁰
				82 (8) ^f						
I-benzene	C ²⁹⁹	1		86 (4)	67 (3)					
anisole	C ²⁹⁸	1	184 (18)	114 (8)	79 (3)	72 (4)	66 (5)			236 (9) ²⁹⁰
	C ²⁹⁸	2	122 (4)	89 (2)	70 (3)	64 (3)	62 (4)			
	C ³⁰¹	1	205 (9)	121 (3)	100 (4)	90 (3)	82 (3)			248 (8) ²⁹⁰
indole	A ²⁹⁷			138 (14)	105 (13)			201 (20)	201 (20)	
	C ³⁰¹	2	120 (5)	97 (3)	79 (3)	73 (3)	69 (3)			
	C ³⁰²	1	187 (16)	107 (5)	81 (5)	73 (5)	69 (5)			232 (9) ²⁹⁰
naphthalene			165 (11) ^d							
	C ³⁰²	2	117 (4)	91 (3)	75 (3)	70 (4)	65 (3)			

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. ^bReferences for this row except as noted. A = radiative association kinetics,^{291,297} C = threshold collision-induced dissociation,^{118,213,227,290,292,294–296,298–302} E = single temperature equilibrium,^{12,16,113,116,291,293,303} and H = High pressure temperature-dependent equilibrium.^{111,279} ^cCalculated here using the equilibrium value for pyrrole–benzene exchange of 23 kJ/mol from ref 291. ^dRelative free energy from ICR equilibrium (E) at 373 K.^{16,293} Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ Additional $T\Delta S = RT \ln(2) = 2.1$ kJ/mol included here. ^eRelative free energies from ICR equilibrium (E) at 373 K.^{12,113} Adjusted to 0 K in ref 196. Additional $T\Delta S = RT \ln(2) = 2.1$ kJ/mol included here. ^fAdjusted from 298 K ICR free energy (E)¹¹⁶ to 0 K using information in refs 118, 278, 296, and 299.

similar to the $71 \pm 9\%$ found for its congener Cu⁺.²³³ Photodissociation values are also available for one benzene bound to the metal heterodimer cations, MFe^+ , where $M = Sc, V, Co,$ and Nb .²⁸⁶

III.D.2.a. Trends. The trends in the first and second BDEs to the transition metals are notable, as described and amplified more fully elsewhere.²³³ It can be seen that for the early metals, Sc⁺, Ti⁺, and V⁺, the first and second BDEs are similar, whereas for Cr⁺ and Mn⁺ the first bonds are considerably smaller than the second. This can be attributed to a spin change associated with the addition of the second ligand, an effect discussed above. For the late metals, Fe⁺, Co⁺, Ni⁺, Cu⁺, and Ag⁺, the second ligand binds less strongly than the first, a consequence of the 18 electron rule. Past Mn⁺(C₆H₆)₂, which has 18 valence electrons counting benzene as a six-electron donor, the second benzene ligand exceeds this electron count. Thus, the second

ligand binds by an increasingly smaller value, consistent with the second ligand no longer being able to donate six electrons.

One issue in converting the various thermodynamic values available in the literature from free energies to enthalpies concerns the symmetry number. It was recognized early by Staley¹¹⁷ that because the rotational symmetry number of benzene is 12, whereas that for a symmetrically ligated $M^+(C_6H_6)$ complex is 6, there is a $R \ln(2)$ contribution to the dissociation entropy and thus free energy. (Equivalently, this factor of 2 can be viewed as originating from benzene being able to bind on either face.) This factor does not affect the determination of the thresholds for TCID experiments, although Amicangelo and Armentrout included this factor in their analysis of competitive dissociations from bis-ligated $LM^+(C_6H_6)$ complexes.¹⁰⁷ This factor has not been routinely included in previous adjustments of free energy values to

Table 22. Sequential Bond Dissociation Energies (kJ/mol) of $M^+(L)_x$ Complexes for Miscellaneous π -Ligands^a

L	ref ^d	x	Al ⁺	Sc ⁺	Ti ⁺	V ⁺	Cr ⁺	Fe ⁺	
C ₂ H ₂		1	59 (4) ⁹¹	240 (20) ^{306c}	253 (20) ^{307c}	205 (20) ^{308c}	184 (20) ^{309c}	159 (11) ^d	
		2	57 (6) ⁹¹						
L	ref ^d	x	Li ⁺	Na ⁺	Sc ⁺	Ti ⁺	Cr ⁺	Fe ⁺	Co ⁺
C ₃ H ₄	D ⁴⁴	1	116 (15) ^e		256 (20) ^{310c}	251 (14) ^{307c}	140 (7) ^{311c}		134 (25) ³⁰⁴
C ₃ H ₆		1	93 (15) ^e					166 (7) ³¹³	180 (7) ³¹⁴
								155 (21)	184 (21)
								155 (11) ^d	
CH ₂ C(CH ₃) ₂		1	112 (15) ^e	67 (3) ^f				164 (11) ^d	
L	ref ^b	x	V ⁺	Cr ⁺	Mn ⁺	Fe ⁺	Co ⁺	Ni ⁺	
pyrrole	A ²⁹¹	1	>171	178 (21)	177 (21)	226 (21)	>276	>284	
	P					201 (21) ³⁰⁵	247 (13) ³⁰⁴		
	A ²⁹¹	2		146 (21)	113 (21)	174 (21)	194 (21)	197 (21)	
	P ³⁰⁴						<201 (13)		

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. ^bReferences for this row except as noted. A = radiative association kinetics,²⁹¹ C = threshold collision-induced dissociation,^{313,314} D = kinetic energy release distribution,⁴⁴ E = single temperature equilibrium,^{116,187} H = high pressure temperature-dependent equilibrium,⁹¹ K = kinetic method,¹³³ P = photodissociation,^{304,305} and T = threshold of endothermic reaction.^{306–311} ^cValues from thresholds of endothermic reactions (T) reinterpreted and adjusted to 0 K in ref 10. ^dRelative kinetic method values (K)¹³³ anchored to $D(\text{Fe}^+-\text{C}_2\text{H}_4)$ from ref 135. ^eRelative free energy from ICR equilibrium (E) at 298 K¹⁸⁷ reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. Additional $T\Delta S = RT \ln(2) = 1.7$ kJ/mol included here for isobutene. ^fFree energies at 298 K (E)¹¹⁶ and adjusted to 298 K ΔH using ΔS values calculated in this reference. Additional $T\Delta S = RT \ln(2) = 1.7$ kJ/mol included here.

Table 23. Bond Dissociation Energies (kJ/mol) of M^+-L with Miscellaneous Inorganic Ligands^a

L	ref ^b	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Al ⁺
OP(OCH ₃) ₃	C ³¹⁵	281 (15)	172 (6)	135 (4)	124 (6)	103 (4)	
	E ¹³	233 (11) ^c					
OP(OC ₂ H ₅) ₃	C ³¹⁶	224 (11) ^d	181 (6)	135 (6)	130 (5)	121 (5)	
CH ₃ F		125 (15) ^e					89 (8) ^f

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. ^bReferences for this row except as noted. C = threshold collision-induced dissociation,^{315,316} E = single temperature equilibrium,^{12,13,16,113,116,187} and H = high pressure temperature-dependent equilibrium.¹⁸⁶ ^cRelative free energy from ICR equilibrium (E) at 373 K¹³ adjusted to 0 K using information in that reference. ^dRelative free energy from ICR equilibrium (E) at 373 K.^{12,16,113} Adjusted approximately to 0 K by adding $H_0 - G_{373} = 35.4 \pm 2.4$ kJ/mol, determined from comparison of values in ref 196 versus refs 113 and 12. Adjustment is consistent with average $T\Delta S_{373}$ calculated elsewhere.¹³ ^eRelative free energy from ICR equilibrium (E) at 298 K,¹⁸⁷ reanchored here and adjusted approximately to 0 K using the average value for $H_0 - G_{298} = 26.1 \pm 2$ kJ/mol from ref 196. ^fHigh pressure temperature-dependent equilibrium (H)¹⁸⁶ adjusted from 298 to 0 K using information in ref 15.

enthalpies.^{118,119,196,278} Table 20 does include this factor in any values converted from free energies. A similar correction may be needed for other π -complexes (and other symmetric ligands) as discussed below. Ethene falls into this category, but no values in Table 19 required this factor.

III.D.3. Additional π -Ligands: Pyrroles, Substituted Benzenes, and Larger Aromatic Rings. Table 21 lists BDEs for both one and two π -ligands bound to several metal cations, all five alkalis along with Mg⁺, Al⁺, and Cu⁺. Values for pyrrole and 1-methylpyrrole, the five-membered nitrogen heterocycle, $c\text{-C}_4\text{H}_5\text{N}$, have been obtained by TCID methods (C),^{213,227,290} radiative association kinetics (A),²⁹¹ and single temperature equilibrium (E) measurements.²⁹¹ The latter two methods yield values in reasonable agreement as do the C and A values for Cu⁺–pyrrole. The substituted benzenes include methyl,^{290,292,293} amino,^{111,290,294} methylamino,^{290,295} dimethylamino,^{290,295} hydroxy,^{12,113,116,118,296,297} methoxy,^{290,298} and halo.^{116,290,299,300} Larger aromatic ligands include indole^{290,297,301} and naphthalene.^{16,290,302,303} In cases where there are overlapping values, agreement is generally good.

Additional values not included in Table 21 are the lithium cation basicities of many other benzene derivatives and larger aromatic ligands measured by single temperature equilibrium (E).^{16,303} In addition, Cr⁺ bound to toluene, *p*-xylene, and

mesitylene has been determined by radiative association kinetics (A), 177 ± 15 , 180 ± 19 , and 193 ± 29 kJ/mol, respectively for the first ligand, and 222 ± 39 , 212 ± 29 , and 212 ± 39 kJ/mol for the second ligand.²⁸⁷ For benzene, the second ligand binds more strongly by $36 \pm 13\%$, whereas these three ligands show enhancements of 25 ± 24 , 18 ± 20 , and $10 \pm 26\%$, respectively. Values for phenol bound to Cr⁺ and Fe⁺ have been measured by radiative association kinetics (A) as 206 ± 21 and $>238 \pm 24$ kJ/mol, respectively.²⁹⁷ From the same reference, indole bound to Ca⁺ has been determined as 151 ± 15 kJ/mol and lower limits of 201 ± 20 kJ/mol were ascertained for Cr⁺, Fe⁺, and Mo⁺.

III.D.4. Miscellaneous π -Ligands. BDEs of one and two pyrrole ligands to several of the transition metal cations have also been measured and are collected in Table 22 along with several other π -ligands, mainly small alkynes and alkenes. The pyrrole values come primarily from radiative association kinetics (A) measurements²⁹¹ and photodissociation (P).^{304,305} Values for ethyne and propyne binding to transition metal cations are derived from the thresholds for dehydrogenation reactions (T)^{306–311} that have been reinterpreted and adjusted to 0 K subsequently.¹⁰ These values also include $D(\text{Y}^+-\text{C}_2\text{H}_2) = 253 \pm 30$ kJ/mol and $D(\text{La}^+-\text{C}_2\text{H}_2) = 262 \pm 30$ kJ/mol.³¹² Additional values for one and two ethyne ligands

Table 24. Bond Dissociation Energies (kJ/mol) of M⁺(L) Complexes for Amino Acids and Small Peptides^a

L	Li ⁺	Na ⁺	Na ⁺ ^{330b}	K ⁺	Rb ⁺	Cs ⁺	Cu ⁺ ^{340b}	Ag ⁺ ^{341b}
Gly	220 (8) ¹⁹⁶ 224 (10) ^{b,c} 230 (14) ^{b,d}	164 (6) ²¹⁹ 151 (10) ²⁰⁹ 159 (12) ³²⁹	159 (8) 157 (20) ^{322b}	121 (4) ²²⁶ 125 (10) ²⁰⁹ 119 (11) ^{334b} 127 (11) ^{334b} 130 (11) ^{334b} 138 (11) ^{334b}	109 (7) ³³⁶	93 (3) ³³⁷	0	0
GlyOCH ₃	237 (20) ^{b,e}		170 (20) ^{322b}					
Sar	232 (20) ^{b,e}							
Bet								
Ala	229 (20) ^{b,e} 239 (17) ^{b,f}	167 (12) ³²⁹	165 (8) 163 (20) ^{322b}	123 (11) ^{334b}			7 (1)	6 (1)
homoAla	233 (20) ^{b,e}		167 (20) ^{322b}	127 (11) ^{334b}				
Val	238 (20) ^{b,e} 247 (17) ^{b,f}	171 (12) ³²⁹	171 (8) 170 (20) ^{322b}	127 (11) ^{334b}			15 (1)	10 (1)
Leu	248 (17) ^{b,f}		172 (8)	128 (11) ^{334b}			17 (1)	10 (1)
Ile	248 (17) ^{b,f}		174 (8)	129 (11) ^{334b}			18 (1)	12 (1)
Cys	256 (12) ³¹⁷ 245 (14) ^{b,d}	177 (5) ³¹⁷ 177 (12) ³²⁹	174 (8)	121 (3) ³¹⁷	102 (3) ³¹⁷	97 (4) ³³⁷		
Pro	255 (7) ³¹⁸ 253 (14) ^{b,d}	186 (5) ³²¹ 174 (12) ³²⁹	194 (8)	144 (4) ³²¹	125 (5) ³³⁶	108 (5) ³³⁷	20 (1)	21 (1)
Aze	226 (14) ^g	177 (5) ³²¹		132 (5) ³²¹				
Pip	248 (16) ^g	184 (6) ³²¹		135 (5) ³²¹				
N-CH ₃ Aze				165 (14) ^h				
N-CH ₃ Pro	264 (13) ³¹⁸	194 (9) ³²⁵		155 (6) ³²⁵	130 (6) ³²⁵			
N-CH ₃ Pip				159 (14) ^h				
Asp	274 (17) ^{b,f}	195 (6) ³²⁶	201 (8) 199 (8) ^{331b}	148 (7) ³³³	126 (7) ³³⁸	109 (7) ³³⁸	21 (1)	13 (1)
Glu	280 (17) ^{b,f}	199 (5) ³²⁶	202 (8) 201 (8) ^{331b}	152 (7) ³³³	134 (8) ³³⁸	113 (7) ³³⁸	30 (1)	19 (1)
Ser	281 (13) ³¹⁹ 261 (14) ^{b,d}	200 (8) ³¹⁹ 185 (12) ³²⁹	189 (8)	145 (7) ³¹⁹	116 (5) ³³⁶	102 (4) ³³⁷	13 (1)	13 (2)
Met	292 (12) ³²⁰ 274 (14) ^{b,d}	202 (11) ³²⁰		142 (11) ³²⁰	121 (7) ³³⁹	103 (7) ³³⁹	44 (1)	55 (1)
Thr	285 (14) ³¹⁹ 272 (14) ^{b,d}	204 (10) ³¹⁹	195 (8)	149 (10) ³¹⁹	122 (5) ³³⁶	105 (4) ³³⁷	19 (1)	19 (1)
Phe	261 (17) ^{b,f}	206 (7) ³²⁷ 195 (12) ³²⁹	196 (8)	150 (6) ³²⁷	124 (7) ³³⁹	113 (6) ³³⁹	33 (1)	40 (1)
Tyr	264 (17) ^{b,f}	209 (10) ³²⁷	198 (8)	155 (9) ³²⁷	126 (7) ³³⁹	116 (7) ³³⁹	35 (1)	40 (1)
Asn		209 (6) ³²⁶	205 (8) 215 (8) ^{331b}	156 (7) ³³³	138 (7) ³³⁸	115 (7) ³³⁸	28 (1)	35 (1)
Gln		213 (6) ³²⁶	209 (8) 219 (8) ^{331b}	161 (8) ³³³	144 (9) ³³⁸	128 (9) ³³⁸	41 (1)	45 (1)
Trp	277 (17) ^{b,f}	217 (8) ³²⁷ 202 (12) ³²⁹	207 (8)	165 (6) ³²⁷	138 (8) ³³⁹	125 (7) ³³⁹	47 (1)	61 (1)
Lys			>211 (8) >211 (8) ^{331b}				>56 (1)	83 (5)
His		222 (11) ³²⁸ 183 (12) ³²⁹	217 (8) 225 (8) ^{331b}	164 (9) ³²⁸	137 (6) ³²⁸	118 (6) ³²⁸	56 (1)	75 (4)
Arg			>223 (8) 240 (8) ^{331b}				>56 (1)	>112
Gly ₂		209 (13) ³⁶⁵ 179 (10) ²⁰⁹ 184 (16) ^{367b}	201 (8) ^{332b} 175 (10) ^{366b} 184 (16) ^{367b}	149 (7) ³⁶⁵				
Gly ₃		240 (17) ³⁶⁵	236 (9) ^{332b}	183 (15) ³⁶⁵				
Gly ₄			261 (11) ^{332b}					

^aUncertainties in parentheses. Sar = sarcosine = N-CH₃Gly, Bet = N,N-(CH₃)₂Gly, homoAla = α-aminobutyric acid, Aze = azetidine-2-carboxylic acid, and Pip = pipercolic acid. C = threshold collision-induced dissociation,^{196,209,219,226,317–321,325–328,333,336–339,365} K = kinetic method results,^{322–324,331,332,334,340,341,366,367} and E = single temperature equilibrium.³²⁹ ^bK = kinetic method results. ^cExtended kinetic method results (K) anchored to experimental values of the references.³²⁴ If theoretical G4 values for the references are used, the value becomes 231 ± 3 kJ/mol. ^dKinetic method results (K) at 373 K,³²³ reanchored here and adjusted to 0 K using information calculated in refs 317–320 and 324. ^eKinetic method results (K)³²² reanchored here to D₀(Li⁺–Gly) = 222 (8) kJ/mol. ^fKinetic method results (K) at 373 K,³²³ reanchored here and adjusted approximately to 0 K using ΔH₀ – ΔG₃₇₃ = 43.7 ± 4.0 kJ/mol. See text. ^gRelative values (C),³²¹ readjusted to absolute value for Pro that accounts for competitive shift reported in ref 318. Original values were 279 (10) kJ/mol for Pro, 250 (14) kJ/mol for Aze, and 272 (16) kJ/mol for Pip. ^hRelative values obtained from kinetic studies under IRMPD irradiation,³³⁵ reanchored to value for N-CH₃–Pro in ref 325.

bound to Al^+ come from high pressure temperature-dependent equilibria (H),⁹¹ and those for propyne and propene bound to Li^+ come from relative free energy measurements (E) in an ICR (adjusted as described in Table 22),¹⁸⁷ and a photodissociation (P) threshold yielding propyne (possibly allene) bound to Co^+ .³⁰⁴ In addition, for propene, values for Fe^+ and Co^+ have been measured using kinetic energy release distributions (D),⁴⁴ with values that agree well with those from TCID (C) measurements^{313,314} and to a kinetic method (K) result.¹³³ The latter work also includes the values for ethyne and isobutene in Table 22 along with $D(\text{Fe}^+-\text{C}_4\text{H}_6) = 182 \pm 11$ kJ/mol. Isobutene bound to Li^+ and Na^+ have also been determined using ICR equilibria (E).^{116,187} In both of these cases, the values have been adjusted by including an $R \ln(2)$ factor in ΔS , as discussed above.

III.E. Miscellaneous Inorganic Ligands

The tables above do not include many additional ligands for which there are few values for comparison or for multiple metal centers. Of the few additional ligands that do meet these criteria, Table 23 lists the values available. These include trimethyl and triethyl phosphate, $\text{OP}(\text{OCH}_3)_3$ and $\text{OP}(\text{OC}_2\text{H}_5)_3$, for which the alkali cation affinities have been measured using TCID (C) methods.^{315,316} Additional values for trimethyl phosphate can be obtained from ICR equilibrium studies (E), both the original values from Taft and co-workers^{12,16,113} and those reexamined by Mayeux et al.¹³ The former lies 25 kJ/mol below the latter and is not included in Table 23. The revised ICR value, which still lies well below the TCID value, agrees better with theoretical calculations.^{13,315} It seems likely that the ICR value for triethyl phosphate is also in need of reevaluation as all other metal cations bind $\text{OP}(\text{OC}_2\text{H}_5)_3$ more strongly than $\text{OP}(\text{OCH}_3)_3$, whereas the two ICR values for Li^+ are inverted. In addition, Table 23 includes BDEs for Li^+ and Al^+ bound to CH_3F . The former is another ICR equilibrium measurement (E)¹⁸⁷ approximately adjusted to 0 K here, whereas the latter was determined by high pressure temperature-dependent equilibrium (H).¹⁸⁶

For other ligands, lithium ion basicities have been determined using ICR equilibrium for many alkyl halides, and some of these are also available for sodium ion basicities.¹⁶ Keese and Castleman have listed some additional values of potential interest.⁵

III.F. Biological Systems

III.F.1. Metalated Amino Acids. Table 24 lists values for the metal cation affinities of amino acids that have been determined predominantly using either the kinetic method (K) or threshold collision-induced dissociation (TCID, C). For the former results to be meaningful, the relative values measured need to be anchored properly and considerable entropic effects should be accounted for. The latter yields absolute affinities directly and, as presently constituted, includes all known entropic effects.^{33,36} Such differences can probably explain discrepancies in the relative values obtained by the two methods, as described further below.

III.F.1.a. Lithium. Absolute lithium cation affinities of several amino acids along with azetidine-2-carboxylic acid (Aze), the four-membered-ring analogue of proline, pipecolic acid (Pip, the six-membered-ring analogue of proline), and *N*-methylproline are available from TCID (C) studies.^{196,317–321} These studies are made difficult by several considerations that do not plague similar studies of heavier metal cations. (a) The lithium cation affinities are sufficiently strong that loss of the amino

acid ligand (AA) to form $\text{Li}^+ + \text{AA}$ competes with other decomposition pathways resulting from covalent bond cleavages of the ligand. (b) Efficient collection of the light lithium cation requires careful setting of the analysis mass filter. Although most of the TCID values in Table 24 were interpreted including the effects of competition in the original papers, a recent reanalysis of the data for $\text{Li}^+(\text{Pro})$ ³¹⁸ shows that competition increased the apparent BDE originally reported³²¹ by 24 kJ/mol. Table 24 includes this correction for the $\text{Li}^+(\text{Aze})$ and $\text{Li}^+(\text{Pip})$ values from this reference as well.

Bojesen et al.³²² utilized the kinetic method (K) to study the relative lithium cation affinities of the aliphatic amino acids, with additional qualitative information obtained for most amino acids. They could observe competitive dissociation of an $(\text{Ala})\text{Li}^+(\text{DMF})$ complex, where DMF is *N,N*-dimethylformamide. Thus, they anchored their relative values to the lithium cation affinity of DMF, using a value of 209 kJ/mol, apparently from the work of Taft et al.^{12,113} The resultant value for $\text{Li}^+(\text{Gly})$ adjusted to 0 K¹⁹⁶ is 211 ± 12 kJ/mol, within experimental uncertainty but below the other values in the literature (Table 24). This could easily be because of entropic effects associated with the differences between DMF (monodentate) and Ala (bidentate). The values shown in Table 24 from Bojesen et al. have been reanchored here to the 0 K $\text{Li}^+(\text{Gly})$ results (taking an average value of 222 kJ/mol).

Feng, Gronert, and Lebrilla also used the kinetic method to measure relative lithium cation basicities at 373 K of the amino acids.³²³ They analyzed data for pairs of amino acids as well as amino acids relative to dimethoxyethane (DXE) and diethoxyethane, with the absolute scales set by using values for DMF, *N*-methylacetamide, and *N,N*-dimethylacetamide, and DXE from Burk et al.¹² As noted above, all of these values have subsequently been revised¹³ such that the scale determined by Feng et al. should be systematically increased by 14.8 kJ/mol. This still leaves the results as free energies at 373 K; however, corrections to 0 K enthalpies have been explicitly calculated for Gly²⁷⁶ and Cys.³¹⁷ For Pro, Ser, Thr, and Met, $\Delta H_0 - \Delta G_{298}$ values have been explicitly calculated^{319–321} and here we assume that $\Delta H_0 - \Delta G_{373} \sim \Delta H_0 - \Delta H_{298} + 373\Delta S_{298}$ (which is true for Li^+Cys within 0.1 kJ/mol) for these complexes. For all other amino acids examined by Feng et al., relative free energies are adjusted to 0 K using the average value for $\Delta H_0 - \Delta G_{373}$ of 43.7 ± 4.0 kJ/mol. This leads to values from Feng et al. that are within experimental uncertainty of all TCID values.

Very recently, Bouchoux et al. utilized the extended kinetic method to measure the lithium cation affinity of glycine.³²⁴ References included DMF, dimethyl sulfoxide, *N*-methylacetamide, *N,N*-dimethylacetamide, 2,4-pentanedione, and trimethyl phosphate, with values taken from the revised scale of Mayeux et al.¹³ An appreciable entropy effect is observed and attributed to the bidentate nature of Gly binding relative to the monodentate references. The relative free energy value obtained at 373 K is adjusted here to 0 K using theoretical information, yielding 224 ± 10 kJ/mol (where the reported uncertainty of ± 2 kJ/mol has been increased to include the ± 9.3 kJ/mol uncertainty in the absolute reference values), which agrees well with the TCID result of 220 ± 8 . These authors also use lithium cation affinities calculated at the G4 level for their reference molecules to obtain $D_0(\text{Li}^+-\text{Gly}) = 231 \pm 3$ kJ/mol, which not surprisingly agrees better with their G4 calculated value of 237 kJ/mol.

III.F.1b. Sodium. TCID methods (C) have been used to measure the sodium cation affinity of Gly in two laboratories: 151 ± 10^{209} and 164 ± 6^{219} kJ/mol. Reasons for the discrepancy between these values has been discussed²¹⁹ and are partially attributable to pressure effects (uncorrected for in the earlier study) and possible differences in the temperatures of the ions. Additional TCID values are available for 14 other amino acids along with *N*-CH₃Pro, Aze, and Pip.^{317,319–321,325–328} Gapeev and Dunbar examined 10 amino acid complexes with Na⁺ using single temperature ligand exchange equilibria (E) relative to pyridine, AlaOCH₃, and ValOCH₃ (temperatures ranging from 298 to 393 K).³²⁹ Their corrections from ΔG_T at the experimental temperature to ΔH_{298} included entropy contributions from the changes in rotation, vibration, and translation upon dissociation (as per usual) but also contributions from the conformations accessed by the reactants and products at their equilibrium temperature. The latter contributions average 10 J/K mol (or $T\Delta S = 3$ kJ/mol at 298 K). They anchored their relative scale to a value for $D_{298}(\text{Na}^+ - \text{Gly}) = 161 \pm 8$ kJ/mol from Kish et al. (see below) and assign an overall uncertainty in their absolute values of ± 12 kJ/mol. In Table 24, we have adjusted these 298 K values to 0 K by subtracting 2 ± 1 kJ/mol, the average of computed correction values for these complexes found both by Gapeev and Dunbar (2 ± 1 kJ/mol) and in our work on these systems (2.1 ± 0.5 kJ/mol). Additional values include AlaOCH₃ (174 ± 12 kJ/mol) and ValOCH₃ (177 ± 12 kJ/mol). Compared with the TCID values (Gly, Cys, Pro, Ser, Phe, and Trp), the values lie an average of 10 ± 6 kJ/mol lower, a discrepancy that is halved if the values are anchored to the TCID value of $D_0(\text{Na}^+ - \text{Gly}) = 164 \pm 6$ kJ/mol.²¹⁹ The value for Na⁺(His) is clearly much too low, which Gapeev and Dunbar attribute to the possible presence of a low-affinity tautomer of His in their experiments.

Bojesen et al.³²² utilized the kinetic method (K) to study the relative sodium cation affinities of several aliphatic amino acids, with additional qualitative information obtained for most amino acids. Having no absolute anchor for their sodium cation affinities, they simply used a value for Ala that was 75% of the lithium cation affinity scale. In this case, the resultant values agree reasonably well with others in the literature for Na⁺(Gly), and hence the values reported in Table 24 are unchanged. Their absolute values were assigned a large uncertainty of 20 kJ/mol, but generally agree well with the values obtained by Wesdemiotis and co-workers, who provided a more extensive scale of sodium cation affinities for the amino acids using the kinetic method (K).^{330,331} In their initial study,³³⁰ their absolute scale was determined by obtaining the relative affinity at four different collision energies covering an effective temperature range of 378–487 K for alanine (Ala) versus 298 K values for acetamide and its mono and bis *N*-methyl derivatives taken from Kebarle's work (C).²⁰⁹ The value obtained, $D_{298}(\text{Na}^+ - \text{Ala}) = 166.8 \pm 8$ kJ/mol, is then combined with relative affinities for pairs of amino acids. This ladder of affinities was self-consistent except for the sodium cation bound dimers of Lys and Trp, Arg and His, and Pro and Tyr, which exhibited anomalous behavior attributed to entropic effects. Here, values from this work have been adjusted to 0 K values either using $\Delta H_{298} - \Delta H_0$ values taken from theory calculated in the TCID work for that amino acid or using the average adjustment of 2 ± 1 kJ/mol discussed above. In a subsequent study,³³¹ amino acids that bind more tightly were reexamined (K) using small peptides as the reference

species.³³² Here the effective temperature was 354 ± 30 K. Relative to Pro, sodium cation affinities from the two studies for Thr, Phe, and Trp were the same, those for Asp and Glu dropped by 1–2 kJ/mol, and those for the tightly bound Asn, Gln, and His increased by about 10 kJ/mol. Both values are included in Table 24.

Figure 8 shows a comparison of the various values determined for the sodium cation affinities of the amino acids

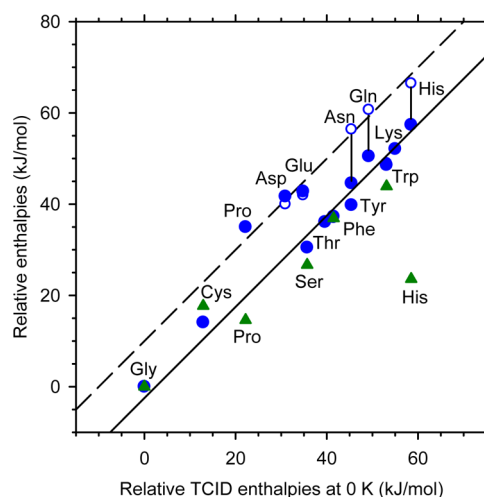


Figure 8. Sodium cation enthalpies of binding to amino acids relative to the value for glycine (Gly). Values from kinetic method (K, blue circles, solid³³⁰ and open³³¹) and single temperature equilibrium (E, green triangles³²⁹) experiments are shown versus threshold collision-induced dissociation (TCID, C) values. All values were taken from Table 24. The solid line shows a linear regression analysis constrained to a slope of unity for the blue circles excluding Pro, Asp, and Glu. The dashed line also has a slope of unity and has been displaced upward by 12.5 kJ/mol.

in a way that emphasizes the relative values. All data is referenced to the value for Na⁺(Gly). It should be kept in mind that the TCID measurements are all completely independent from one another, in contrast to those from Gapeev and Dunbar (equilibrium = E, triangles) and Wesdemiotis and co-workers (kinetic method = K; original data set, closed circles; revised data set, open circles). The lower line is a best fit to the TCID versus K(original) excluding Pro, Asp, and Glu with a slope of unity. It is displaced from passing through the origin by 2.5 kJ/mol, well within the uncertainty of either method. This correlation clearly indicates that the relative values determined by the two methods are in very good agreement with the exception of the three outliers. Notably the equilibrium values from Gapeev and Dunbar also parallel this line with the exception of His. The K(revised) values move the Asn, Gln, and His values upward so that, along with Pro, Asp, and Glu, they form a separate set of values that lies 10 kJ/mol above a line that passes through the origin (dashed line). Again the relative values of these six amino acids now parallel those obtained by TCID. Overall, this comparison shows that the various values obtained by TCID (C), the kinetic method (K), and equilibrium (E) are in good agreement within their stated uncertainties. It probably emphasizes the fact that relative values from the kinetic method may not actually be more accurate than those from other methods as entropic effects are usually not accounted for and can easily cause shifts of 10 kJ/

mol or more. As noted above, the TCID analysis should not be subject to such systematic uncertainties.

III.F.1.c. Potassium. Many of the absolute potassium cation affinities of amino acids have been measured using TCID methods (C).^{209,226,317,319–321,325,327,328,333} Here the early value of Kebarle and co-workers for $K^+(\text{Gly})$, 125 ± 10 kJ/mol,²⁰⁹ agrees within experimental uncertainty with the more recent value from Moision and Armentrout, 121 ± 4 kJ/mol.²²⁶ Tsang and co-workers have used the kinetic method (K) to determine the K^+ relative affinities of the aliphatic amino acids and various methyl derivatives.³³⁴ Potassium ion affinities of acetamide and its *N*-methylated derivatives taken from theory²²² and validated by TCID experiments of Kebarle and co-workers²⁰⁹ were used as reference bases and as 0 K anchors to the relative scale. No explicit entropic effects were included, such that the authors consider their relative basicity scale to translate directly to the relative affinity scale. Notably, they obtain a value for $K^+(\text{Gly})$ (the only amino acid where the kinetic method and TCID values overlap) that matches the TCID experimental values well.^{209,226} Not included in Table 24 are values for *N*-methylated Ala, Val, Leu, and homoAla (α -amino butanoic acid).³³⁴ Relative values for *N*-methylated Pro and its smaller and larger ring analogues (*N*-CH₃Aze and *N*-CH₃Pip) were also measured using a novel study of the kinetics for dissociation upon infrared multiple photon dissociation (IRMPD) irradiation³³⁵ and anchored via TCID studies of *N*-CH₃Pro.³²⁵

III.F.1.d. Rubidium and Cesium. Values for the amino acid affinities of rubidium and cesium cations have come exclusively from threshold collision-induced dissociation measurements (C).^{317,325,328,336–339} These values follow the same overall trends with amino acid found for the better studied lighter alkali cations with binding energies that are weaker, consistent with their larger ionic radii (see section III.B.6.a).

III.F.1.e. Copper and Silver. Table 24 also includes relative affinities of many of the amino acids to Cu^+ and Ag^+ . Cerda and Wesdemiotis used the kinetic method (K) to determine relative Cu^+ affinities,³⁴⁰ assigning an effective temperature of 508 ± 10 K on the basis of results for proton bound dimers of the amino acids. Their results did not include direct consideration of entropic effects, and the values in Table 24 are most conservatively viewed as relative free energies but can be reduced to relative enthalpies if relative entropic effects are small. Siu and co-workers measured the Ag^+ relative affinities using the kinetic method (K),³⁴¹ obtaining self-consistent results for all amino acids except Lys, His, and Arg, which they suggest is a result of entropic effects that are not explicitly considered. The relative values reported in Table 24 are best viewed as relative free energies at an effective temperature estimated to be 902 ± 26 K. As long as the entropic effects are comparable, these relative values can probably be converted to relative enthalpies, with such a conversion being more questionable for Lys, His, and Arg. These authors compare their relative affinities to those for Cu^+ finding that most amino acids bind less strongly to Ag^+ , an effect of the larger ionic radius, whereas those with nitrogen- or sulfur-containing or aromatic side chains have larger relative affinities than Cu^+ , using hard–soft acid–base concepts to rationalize the results.

III.F.1.f. Trends. In order to better understand how metal cations bind to the simplest amino acid, glycine, Moision and Armentrout “dissected” the interaction by examining the binding energies of Na^+ and K^+ with comparably sized molecules containing only one (propanol, propyl amine, and

methyl ethyl ketone) or two (propionic acid, 2-aminoethanol, and 1-amino-2-propanone (theory only)) of the functional groups of Gly.^{219,226} Comparison of these data shows that the carbonyl group binds more tightly than the hydroxy or amino group, with Na^+ binding the amine more tightly than the alcohol, but K^+ binding the alcohol more strongly than the amine. Propionic acid binds the metal cations less tightly than the ketone, indicating that the hydroxyl group withdraws electron density from the carbonyl (an effect also noted in section III.C.1.i). The strongest bonds are made to glycine along with 2-aminoethanol and 1-amino-2-propanone, because these are all bidentate ligands. They have comparable binding energies, with Gly somewhat weaker than the other two ligands (by 11 kJ/mol for Na^+ and 5 kJ/mol for K^+).

The effects of the side chain on the binding to amino acids have also been explored. As first noted by Ruan and Rodgers,³²⁷ the binding energies of alkali metal cations to the amino acids having aromatic side chains correlate nicely with the polarizability of the amino acid. This correlation has been extended in subsequent work, which shows the same qualitative trends for all the alkali metal cations.^{11,328} The correlation shown in Figure 9 for sodium cation affinities is updated further. Here

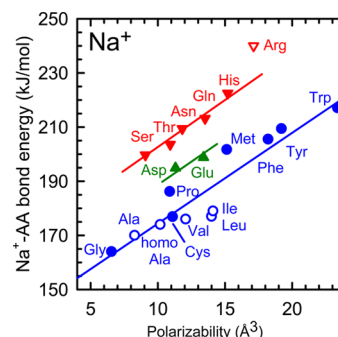


Figure 9. Sodium cation affinities of the amino acids versus their polarizability. Values from TCID studies (Table 24) are shown as solid symbols. Open symbols provide values taken from kinetic method results³³⁰ anchored to the TCID value for $\text{Na}^+(\text{Gly})$, along with the kinetic method result for $\text{Na}^+(\text{Arg})$.³³¹ The blue line shows a linear regression analysis of the solid blue circles. Green and red lines retain the same slope as the blue line but are arbitrarily displaced upward by 15 and 30 kJ/mol, respectively.

the polarizabilities used are taken from experimental results in solution³⁴² except for homoAla, which is taken as the average of the values for Ala and Val. The sodium cation BDEs are TCID results^{219,317,319–321,326–328} (C, solid symbols) when available. Kinetic method results (K, open symbols) are included for the aliphatic side chains³³⁰ and homoAla,³²² where the relative values are anchored to the TCID value for $\text{Na}^+(\text{Gly})$, and arginine (Arg).³³¹ It can be seen that many of the amino acids (shown in blue) correlate well with the polarizability; in particular, Gly, Ala, homoAla, Cys, Phe, Tyr, and Trp form a series that is predictive. The longer chain aliphatic side chains, Val, Leu, and Ile, are on the low side compared with this prediction, whereas Pro and Met are slightly higher. It is also possible that the aliphatic side chains define the primary effect of increasing polarizability, which would mean that Pro, Met, Phe, Tyr, and Trp are enhanced compared to that trend by interaction with the functional groups of the side chains or, in the case of Pro, by the zwitterionic character of this complex. Contributions from the side chain are clear for the other amino

acids, shown in green and red. As discussed elsewhere, Ser, Thr, Asn, Gln, and His have binding affinities that are strongly enhanced but parallel compared to the polarizability trend, which is attributed to additional contributions from the dipole moment of the side chain. This is plausible as Asp and Glu (in green) form a separate correlation in between, which is consistent with the difference between the carboxylic acid group (where the hydroxyl group is electron withdrawing from the carbonyl binding site) and the amide group (where the NH_2 group is not electron withdrawing).

III.F.1.g. Structures. Although space here does not allow a full description of the structures of metalated amino acid complexes, these have been explored thoroughly using theoretical methods coupled with infrared multiple photon dissociation (IRMPD) action spectroscopy (Gly,³⁴³ Pro,^{343–345} Gln,^{345,346} Trp,^{347,348} Phe,³⁴⁷ Lys,^{349,350} Arg,^{345,351,352} Ser,^{345,353} Val,³⁴⁵ Thr,³⁵⁴ Asp,³⁵⁵ Glu,³⁵⁵ Asn,³⁵⁶ Met,³⁵⁷ and Cys³⁵⁸). In general, the lighter alkali cations (Li^+ and Na^+) bind to the backbone carbonyl and amino group along with the heteroatom (or π -cloud) of functionalized side chains. As the metal gets heavier, the distinction between different binding modes becomes smaller such that multiple conformers of these complexes are often observed. An important binding mode becomes complexation to the oxygen atoms of the carboxylic acid group along with the side chain. Generally, the complexes are charge-solvated rather than zwitterionic species, although the cyclic Pro (along with Aze and Pip) and Arg prefer zwitterionic complexes. Evolution in the structures of these complexes has been summarized recently.^{359,360} Structural information for complexes of amino acids with additional metal cations can also be found and is not included here because there is no concomitant thermodynamic information available.³⁶⁰

III.F.1.h. Related Systems. The kinetic method has also been utilized to determine the alkali metal cation binding affinities of amino acids (AA) relative to their methyl esters (AAOCH_3) for Li^+ , Na^+ , K^+ , and Cs^+ .³⁶¹ In general, the esters bind more strongly for the lighter alkalis, whereas the opposite trend is observed for Cs^+ . Proline is an exception, a result of its zwitterionic binding character in the AA form. Lysine with Cs^+ and arginine with K^+ and Cs^+ are also exceptions, again attributable to zwitterionic character.

In novel applications of the TCID method, the BDEs of lithium and sodium cations to fragments of amino acids have also been determined. Interestingly, the thermodynamic information allows unambiguous assignment of the fragment structures by comparison with high level theoretical calculations. Heaton et al.³⁶² determined that sodiated asparagine (Asn) and aspartic acid (Asp) decompose by losing ammonia and water, respectively, forming sodiated 3-amino succinic anhydride, which has a sodium cation affinity at 0 K of 130 ± 5 kJ/mol. Likewise sodiated glutamine (Gln) and glutamic acid (Glu) lose ammonia and water, respectively, to form oxoproline, where $D_0(\text{Na}^+-\text{O}-\text{Pro}) = 161 \pm 6$ kJ/mol. BDEs for water and ammonia bound to each of these complexes are also determined in this work. Ye and Armentrout determined that water loss from lithiated serine (Ser) forms the three-membered ring aziridine-2-carboxylic acid, which has a lithium ion affinity of 234 ± 10 kJ/mol.³⁶³ Deamidation of lithiated cysteine yields a product having a lithium cation affinity of 224 ± 14 kJ/mol, which compared to theory identifies it as the three-membered ring thiirane-carboxylic acid.³⁶⁴

III.F.2. Metalated Peptides. Absolute thermochemistry has not been measured for many small peptides bound to metal cations, but there are several kinetic method studies (K) of such systems. The best studied system is Na^+GlyGly , which has been studied by both TCID (C) and the kinetic method by multiple groups. Using TCID, Klassen et al.²⁰⁹ measured the BDE of the Na^+GlyGly complex to be 179 ± 10 kJ/mol (adjusted to 0 K using information calculated elsewhere),³⁶⁵ compared to a value of 209 ± 13 kJ/mol reported by Ye and Armentrout.³⁶⁵ This latter work also showed that the difference in values was attributable to assumptions made regarding the transition state for dissociation, tight in the former work and loose in the latter. Using the extended kinetic method, Cerda et al.³⁶⁶ measured the Na^+ binding affinity of GlyGly as 175 ± 10 kJ/mol (adjusted to 0 K elsewhere),³⁶⁵ using nucleobases (adenine, cytosine, and guanine) as references. They found a large entropic change of $27 \text{ J}/(\text{mol K})$ ($T\Delta S = 8$ kJ/mol). This laboratory later utilized several amino acids as reference bases, obtaining 201 ± 8 kJ/mol (adjusted to 0 K elsewhere),³⁶⁵ in good agreement with the more recent TCID value. Feng et al.³⁶⁷ measured the relative free energy for dissociation of Na^+GlyGly using the kinetic method (K) at an estimated effective ion temperature of 350 K, which was converted to $\Delta H_0 = 184 \pm 16$ kJ/mol elsewhere.³⁶⁵ This study used the sodium cation affinity of dimethylacetamide measured by Klassen et al. using TCID²⁰⁹ as their anchor, and it can be remembered that values from this study are low compared to other work (by 30 kJ/mol for Na^+GlyGly and 13 kJ/mol for Na^+Gly).

The peptide ligand systems studied by multiple methods are included in Table 24: GlyGly (Gly_2), GlyGlyGly (Gly_3), and GlyGlyGlyGly (Gly_4). As noted above, there is good agreement between the sodium cation affinities measured most recently by TCID (C)³⁶⁵ and the kinetic method (K)³³² for Gly₂ and Gly₃. Notably, the values for Gly₂ and Asn, which are isomers of one another, are essentially the same. Comparison to Gly shows that the BDEs increase with each additional Gly unit, but with decreasing effect. This is consistent with a decreasing charge density on Na^+ as the number of coordinating ligand sites and with increased steric interactions, i.e., the chelation effects noted above (e.g., Figure 7). Comparable values for K^+ follow the same trend (Table 24). Not included in Table 24 are additional sodium cation affinities from kinetic method studies (K)^{331,332} for several other di- and tripeptides bound to Na^+ and include AlaGly, GlyAla, AlaAla, GlyLeu, GlyPhe, SerGly, PheGly, AlaTrp, TrpAla, AlaGlyGly, GlyHis, AlaAlaGly, AlaAlaAla, LeuGlyPhe, HisGly, GlyHisGly, and AlaAlaAlaAla. The kinetic method has also been used to determine free energies for lithium and sodium cation binding to GlyAA where AA = Gly, Cys, Ala, Ser, Val, Thr, Leu, Phe, Met, Tyr, Glu, Pro, and Trp along with the N-acetylated versions of these amino acids.³⁶⁷

III.F.3. Metalated Sugars. There is limited thermodynamic data available for binding metal cations to sugars. The TCID method (C) has been used to determine the sodium cation affinities at 0 K of arabinose, 171 ± 6 kJ/mol, xylose, 181 ± 6 kJ/mol, glucose, 181 ± 7 kJ/mol, and galactose, 203 ± 7 kJ/mol.³⁶⁸ Combined with theoretical work, these values can also be adjusted to yield values for the two anomeric forms present, α and β . The trends in these values are determined by several factors including multidentate Na^+ binding coupled with whether a favored boat ring conformation in the sugar can be

achieved along with the number of hydrogen bonds that stabilize the sodiated monosaccharide structures.

Sodium cation affinities for these and several additional sugars have also been determined using the kinetic method (K), with nucleobases and dipeptides used as references.³⁶⁹ For the four sugars also measured using TCID, the kinetic method yields values of 168, 169, 172, and 175 ± 7 kJ/mol, respectively (after adjustment to 0 K).³⁶⁸ Note that the relative order of these values matches the TCID results, but the range of the values is much less (7 versus 32 kJ/mol). The latter range matches theoretical calculations much better, indicating the kinetic method scale is probably compressed.³⁶⁸ Additional values (at 298 K) include those for the monosaccharides, ribose (176 ± 7 kJ/mol) and mannose (179 ± 7 kJ/mol), and disaccharides, melibiose (198 ± 7 kJ/mol), gentiobiose (201 ± 7 kJ/mol), and lactose (204 ± 7 kJ/mol). In both studies, pentoses bind more weakly than hexoses which bind more weakly than disaccharides.

III.F.4. Metalated Nucleobases. Thermodynamic measurements associated with the DNA and RNA nucleobases, adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U), have been reported for several alkali cation systems. Binding energies were first reported using the kinetic method (K) for Li^+ , Na^+ , and K^+ .³⁷⁰ Reference bases were Gly, Ala, and Val for Li^+ and Na^+ ,³²² and pyridine, *n*-propylamine, and aniline for K^+ .¹¹¹ They also compared relative affinities between pairs of nucleobases, generally obtaining results in agreement within 4 kJ/mol although deviations up to 8 kJ/mol were also observed. As discussed above, the lithium cation affinities from Bojesen et al.³²² have since been revised because the anchors they used (from Taft et al.) have been reevaluated. This was recognized in a subsequent TCID study in which the values from Cerda and Wesdemiotis were revised and adjusted to 0 K.³⁷¹ Here, we use the adjusted values of Bojesen et al. listed in Table 24 as reference values for the Li^+ scale (which increases the values used by Cerda and Wesdemiotis by 9 kJ/mol), and note that the values used by Bojesen et al. for Na^+ agree well with other independent measurements. After adjusting to 0 K values using information calculated elsewhere for A, C, U, and T (for G, the $\Delta H_{298} - \Delta H_0$ values are estimated as 3, 1, and 1 kJ/mol for Li^+ , Na^+ , and K^+) and properly propagating uncertainties,³⁷¹ the values obtained are those listed in Table 25.

TCID studies (C) provide absolute affinities for the same three alkali metal cations bound to A, C, U, and T,^{371–373} but not to G. Notably the cytosine system has been examined twice, originally using a flow tube ion source in which kinetically trapped excited tautomers of the $\text{M}^+(\text{C})$ complexes are formed (as identified by comparison with theory)³⁷² and then using an electrospray source that generates the ground tautomer.³⁷³ In the earlier work, the values obtained correspond to metal binding to the N1 and O2 positions of the C_3 tautomer of cytosine in which the hydrogen on N1 has shifted to O2. In the later work, the metal cations bind to the ground C_1 tautomer at the O2 and N3 sites. This work also includes values for $\text{Rb}^+(\text{C}_1)$ (148 ± 4 kJ/mol) and $\text{Cs}^+(\text{C}_1)$ (137 ± 4 kJ/mol). Comparison of these values shows that the C_1 tautomer binds more tightly than the C_3 tautomer, consistent with theory. Notably, the values obtained from the kinetic method match the $\text{M}^+(\text{C}_3)$ values for Li^+ and Na^+ , whereas that for K^+ is weaker, which may indicate yet another tautomer (C_2 or C_4) is accessed in these experiments. For the other nucleobases, A, U, and T, the kinetic method and TCID

Table 25. Bond Dissociation Energies (kJ/mol) of Metalated Nucleobases^a

nucleobase	ref ^b	Li^+	Na^+	K^+
A	C ³⁷¹	226 (6)	140 (4)	95 (1)
	K ^{370c}	231 (20)	169 (10)	104 (12)
C	C ^{373d}		210 (5)	162 (5)
	C ^{372e}	235 (7)	178 (5)	136 (4)
	K ^{370c}	237 (20)	176 (10)	110 (12)
G	K ^{370c}	245 (20)	181 (10)	116 (12)
U	C ³⁷¹	212 (6)	135 (3)	104 (3)
	K ^{370c}	218 (20)	140 (10)	100 (12)
m ¹ U	C ³⁷⁴	234 (7)	151 (4)	111 (3)
m ³ U	C ³⁷⁴	221 (7)	144 (4)	108 (3)
m ⁵ U (=T)	C ³⁷¹	210 (7)	135 (4)	104 (4)
	K ^{370c}	222 (20)	143 (10)	101 (12)
m ⁶ U	C ³⁷⁴	222 (7)	137 (6)	109 (5)
m ^{1,3} ₂ U	C ³⁷⁴	240 (8)	154 (5)	119 (3)
m ^{5,6} ₂ U	C ³⁷⁴	234 (7)	137 (5)	113 (3)
f ⁵ U	C ³⁷⁵	199 (5)	149 (4)	110 (4)
cl ⁵ U	C ³⁷⁵	243 (8)	141 (3)	104 (3)
cl ⁶ U	C ³⁷⁵	230 (8)	140 (4)	98 (2)
br ⁵ U	C ³⁷⁵	236 (5)	142 (5)	110 (2)
i ⁵ U	C ³⁷⁵		148 (6)	118 (5)
S ² U	C ³⁷⁶	216 (6)	140 (3)	103 (3)
m ⁵ S ² U	C ³⁷⁶	213 (6)	142 (6)	101 (3)
m ⁶ S ² U	C ³⁷⁶	222 (6)	144 (4)	107 (4)
S ⁴ U	C ³⁷⁶	213 (5)	126 (5)	97 (6)
S ^{2,4} ₂ U	C ³⁷⁶	175 (5)	100 (6)	81 (3)

^aValues at 0 K with 298 K values in italics. Uncertainties in parentheses. A = adenine, C = cytosine, G = guanine, T = thymine, U = uracil; m = methyl, f = fluorine, br = bromine, cl = chlorine, i = iodine, S = sulfur; superscripts indicate the position of substitution. ^bC = threshold collision-induced dissociation;^{371–376} K = kinetic method.³⁷⁰ ^cValues reanchored, adjusted from 298 to 0 K, and adjusted for propagation of error as described in the text. ^dValues for O2N3 binding to the C1 canonical tautomer of C. ^eValues for N1O2 binding to the C3 tautomer of C.

values agree within experimental uncertainties, with the exception of $\text{Na}^+(\text{A})$ where there is a difference of 29 kJ/mol. No obvious explanation for this discrepancy is apparent although the lower TCID value agrees better with theoretical values for this complex.³⁷¹

The TCID approach has also extended these studies to various substituted uracils, including methylated (m),³⁷⁴ halogenated (f, cl, br, i),³⁷⁵ and sulfur-substituted (S).³⁷⁶ Methylation generally enhances the binding affinity, but is sensitive to the position with substitution at N1, N3 > C5, C6 = N1 > N3 = C6 > C5 = C for Li^+ , N1, N3 > N1 > N3 > C5, C6 = C6 > C5 = C for Na^+ , and N1, N3 > C5, C6 > N1 > C6 > N3 > C5 = C for K^+ . Halogenation at C5 or C6 also enhances the binding. Substitution of oxygen by sulfur at the O2 site enhances binding to Li^+ and Na^+ but no effect is seen for K^+ , whereas substitution at O4 decreases the binding for Na^+ and K^+ , but has no effect for Li^+ . Substitution at both positions lowers the binding by $22 \pm 4\%$.

III.F.5. Hydration of Metalated Biological Systems. The hydration energies of a number of alkali metal cationized amino acids (AA), nucleobases, and sugars have been examined, as detailed in Table 26. TCID (C) has been used to examine the hydration up to four water molecules of sodiated glycine (Gly),³⁷⁷ cysteine (Cys),³⁷⁸ and proline (Pro).³⁷⁹ Only the latter system has been examined by another method, high

Table 26. Sequential Hydration Energies (kJ/mol) of Metalated Amino Acids, Nucleobases, and Monosaccharides and Related Derivatives^a

species	ref ^b	x = 1	x = 2	x = 3	x = 4
Metalated Amino Acids					
Li ⁺ (Val)	B ³⁸⁵		~67		
	B ³⁸⁶	85 (3)	59 (3)	53 (6)	
Li ⁺ (AlaOC ₂ H ₅)	B ³⁸⁶	82 (3)	59 (3)	36 (9)	
Li ⁺ (Bet)	B ³⁸⁶	79 (3)	65 (4)	47 (5)	
Li ⁺ (α -CH ₃ -Pro)	B ³⁸⁸	78 (1)			
Li ⁺ (N-CH ₃ -Pro)	B ³⁸⁸	77 (1)			
Li ⁺ (ProOCH ₃)	B ³⁸⁸	80 (1)			
Li ⁺ (Gln)	B	63 (1) ³⁸⁹	36 (1) ³⁹⁰		
Li ⁺ (GlnOCH ₃)	B	63 (2) ³⁸⁹	27 (2) ³⁹⁰		
Li ⁺ (AsnOCH ₃)	B	66 (1) ³⁸⁹	33 (3) ³⁹⁰		
Li ⁺ (AsnOC ₂ H ₅)	B	65 (1) ³⁸⁹	33 (1) ³⁹⁰		
Li ⁺ (Lys)	B ³⁹¹	57 (2)			
Li ⁺ (N α -CH ₃ -Lys)	B ³⁹¹	57 (1)			
Li ⁺ (N ϵ -CH ₃ -Lys)	B ³⁹¹	63 (2)			
Li ⁺ (Orn)	B ³⁹¹	63 (2)			
Li ⁺ (LysOCH ₃)	B ³⁹¹	57 (2)			
Na ⁺ (Gly)	C ³⁷⁷	75 (5)	55 (7)	40 (5)	32 (8)
Na ⁺ (Val)	H ³⁸⁰	66 (2)	51 (2)	46 (3)	
	B	67 (1) ³⁸⁷	~52 ³⁸⁵		
Na ⁺ (Bet)	B ³⁸⁷	62 (1)			
Na ⁺ (AlaOC ₂ H ₅)	B ³⁸⁷	67 (1)			
Na ⁺ (SarOC ₂ H ₅)	B ³⁸⁷	67 (1)			
Na ⁺ (Maiba)	B ³⁸⁷	63 (1)			
Na ⁺ (Pro)	C ³⁷⁹	66 (5)	45 (5)	30 (4)	20 (6)
	H ^{380c}	61 (2)	51 (2)	47 (4)	33 (4)
Na ⁺ (α -CH ₃ -Pro)	B ³⁸⁸	53 (1)			
Na ⁺ (N-CH ₃ -Pro)	B ³⁸⁸	53 (1)			
Na ⁺ (ProOCH ₃)	B ³⁸⁸	58 (1)			
Na ⁺ (Met)	H ³⁸⁰	57 (3)	49 (2)		
Na ⁺ (Phe)	H ³⁸⁰	57 (1)	51 (1)		
Na ⁺ (Gln)	H ³⁸⁰	51 (1)	41 (2)		
	B	53 (1) ³⁸⁹	38 (2) ³⁹⁰		
Na ⁺ (GlnOCH ₃)	B	50 (1) ³⁸⁹	36 (2) ³⁹⁰		
Na ⁺ (AsnOCH ₃)	B	53 (1) ³⁸⁹	35 (1) ³⁹⁰		
Na ⁺ (AsnOC ₂ H ₅)	B	53 (1) ³⁸⁹	35 (1) ³⁹⁰		
Na ⁺ (Cys)	C ³⁷⁸	66 (9)	54 (8)	44 (7)	34 (7)
K ⁺ (Gly)	H ³⁸¹	56 (2)	47 (3)	40 (3)	
K ⁺ (Ala)	H ³⁸¹	54 (3)	46 (2)	41 (3)	
K ⁺ (Val)	H ³⁸¹	53 (3)	47 (3)		
	B ³⁸⁵		~31		
K ⁺ (Met)	H ³⁸¹	51 (3)	45 (4)		
K ⁺ (Pro)	H ³⁸¹	50 (1)	46 (1)	38 (3)	
K ⁺ (Phe)	H ³⁸¹	49 (2)	42 (2)		
Metalated Nucleobases					
Na ⁺ (U)	H ³⁸²	62 (2)	51 (2)		
Na ⁺ (S ² U)	H ³⁸³	68 (4)	49 (2)		
Na ⁺ (S ⁴ U)	H ³⁸³	64 (7)	48 (5)		
Na ⁺ (m ⁶ S ² U)	H ³⁸³	63 (3)	51 (2)	44 (2)	
Na ⁺ (T)	H ³⁸²	61 (2)	51 (2)		
Na ⁺ (C)	H ³⁸²	58 (2)	50 (2)		
Na ⁺ (A)	H ³⁸²	54 (2)	48 (2)		
K ⁺ (U)	H ³⁸²	57 (2)			
K ⁺ (T)	H ³⁸²	57 (1)			
K ⁺ (C)	H ³⁸²	56 (1)			
K ⁺ (A)	H ³⁸²	53 (3)			
Metalated Monosaccharides					
Na ⁺ (Ara)	H ³⁸⁴	57 (2)	43 (2)		
Na ⁺ (Xyl)	H ³⁸⁴	56 (2)	45 (3)		

Table 26. continued

species	ref. ^a	$x = 1$	$x = 2$	$x = 3$	$x = 4$
Metalated Monosaccharides					
Na ⁺ (Rib)	H ³⁸⁴	58 (1)	52 (1)		
Na ⁺ (Glc)	H ³⁸⁴	54 (1)	51 (2)		
Na ⁺ (Gal)	H ³⁸⁴	46 (1)	43 (2)		
K ⁺ (Ara)	H ³⁸⁴	49 (1)			
K ⁺ (Xyl)	H ³⁸⁴	52 (2)			
K ⁺ (Rib)	H ³⁸⁴	53 (2)			
K ⁺ (Glc)	H ³⁸⁴	49 (2)			
K ⁺ (Gal)	H ³⁸⁴	50 (1)			

^aValues are at 0 K (298 K values in italics) unless otherwise noted. Uncertainties are listed in parentheses. Orn = ornithine, Sar = sarcosine = $N\text{-CH}_3\text{-Gly}$, Bet = $N,N\text{-(CH}_3)_3\text{Gly}$, Maiba = $N\text{-CH}_3\text{ } \alpha\text{-aminobutanoic acid}$, A = adenine, C = cytosine, G = guanine, U = uracil, T = thymine = $m^5\text{U}$, m = methyl, S = sulfur; superscripts indicate the position of substitution. Ara = arabinose, Xyl = xylose, Rib = ribose, Glc = glucose, Gal = galactose. ^bB = blackbody infrared radiative dissociation,^{387,389,390} C = threshold collision-induced dissociation,^{377–379} and H = high-pressure temperature dependent equilibrium.^{380–384} ^cAdjusted to 0 K using $\Delta H_{298} - \Delta H_0$ values calculated in ref 379.

pressure temperature dependent equilibrium (HPMS, H),³⁸⁰ which has also been used to study sodiated valine (Val), methionine (Met), phenylalanine (Phe), and glutamine (Gln) (but only up to two waters, three for Val),³⁸⁰ along with potassiated Gly, alanine (Ala), Val, Met, Pro, and Phe (two to three waters),³⁸¹ sodiated (two waters except for dithio-6-methyl uracil, $s^2m^6\text{U}$, where three waters could be attached) and potassiated (one water only) nucleobases,^{382,383} and sodiated (two waters) and potassiated (one water) sugars.³⁸⁴ Blackbody infrared radiative dissociation (BIRD, B) has been used to determine hydration energies for up to three waters attached to lithiated, sodiated, and potassiated Val,^{385–387} the isomers of lithiated (one to three waters) and sodiated (one water) Val (Bet = betaine = $N,N\text{-(CH}_3)_3\text{Gly}$, ethyl ester of Ala = AlaOC_2H_5 , ethyl ester of sarcosine = $N\text{-CH}_3\text{GlyOC}_2\text{H}_5$, and $N\text{-methyl } \alpha\text{-aminobutanoic acid} = \text{Maiba}$),^{386,387} one water bound to lithiated Pro methylated at the α C, N, and O,³⁸⁸ Gln, and the esters of Gln and Asn with one and two waters,^{389,390} and one water bound to lithiated Lys, its methylated versions ($N_\alpha\text{-CH}_3$, $N_\epsilon\text{-CH}_3$, and OCH_3), and ornithine (Orn, where the side chain is shorter by one carbon than Lys).³⁹¹

For systems where multiple methods overlap, there is good agreement between the HPMS and BIRD results for Na⁺(Val) and Na⁺(Gln) (one and two waters), whereas these two methods provide very different values for the second hydration energy of K⁺(Val), although difficulties in the approximate BIRD analysis suggest the values for Na⁺(Val)(H₂O)₂ and Ka⁺(Val)(H₂O)₂ “are almost certainly somewhat lower than the true dissociation energies.”³⁸⁵ The only other system where overlap exists is for hydration of Na⁺(Pro), by both TCID³⁷⁹ and HPMS³⁸⁰ methods. Here results for the first and second hydration enthalpies are in reasonable agreement, but the TCID values are 13–17 kJ/mol lower for the third and fourth waters (notably the only system where the HPMS results were extended to a fourth hydration energy). Theoretical values³⁷⁹ lie in between the two sets of experimental numbers, lying closer to the HPMS values. The discrepancies could be because the ions generated in the TCID work are somewhat hotter than believed or because adiabatic cooling in the sampling of the HPMS cell could lead to less dissociation than expected. It is also possible that the structures could be influenced by the disparate temperature ranges needed to reach equilibrium as the size of the cluster varies. For example, for Na⁺(Pro)(H₂O) _{x} , the temperature ranges used for $x = 1, 2, 3$, and 4 are 400–450, 350–400, 320–340, and 300–320 K, respectively.

For all types of biomolecules, hydration energies decrease as the number of waters increases and as the metal cation affinity for the biomolecule increases. This effect can also be observed for variations in the metal cation, where hydration of Li⁺(AA) is weaker than for Na⁺(AA). In many cases, the first two hydration energies to M⁺(AA) are comparable to those for M⁺(H₂O)₃ and M⁺(H₂O)₄, consistent with the amino acids binding in bidentate configurations. Comparison of the hydration energies of Na⁺(Gly), Na⁺(Pro), and Na⁺(Cys) suggests that the first solvent shells are complete at six, four, and four waters, respectively, where the difference occurs because of the zwitterionic character of Pro and the functionalized side chain of Cys provides an internal solvation site. This binding motif probably persists for most other functionalized amino acids. Examination of the hydration of Val and its isomers shows that Val along with AlaOC₂H₅ and SarOC₂H₅ bind water 4–5 kJ/mol more tightly than betaine (Bet) and Maiba, which is rationalized by the former having charge-solvated structures whereas the latter have zwitterionic salt-bridge structures. Comparison of these values also permits the conclusion that Li⁺(Val) does not change its structure upon addition of one and two water molecules, but the third water induces a change in metal cation coordination to a zwitterionic configuration. For sodiated and potassiated cytosine (C), correlation between the metal cation binding affinities and the hydration enthalpies suggests that a mixture of conformations must be present, as also found in the studies of M⁺(C) discussed above.

III.F.6. Protonated Systems. As noted in the Introduction, studies of noncovalent interactions associated with protonated systems are neglected in the present work because such interactions are often really covalent in nature. However, there are several relatively recent studies associated with biological systems that we believe are of interest in the present context, including the host–guest interactions of the 18-crown-6 polyether with peptides and measurements of base-pairing energies of nucleobases.

III.F.6.a. 18-Crown-6 Complexes of Protonated Amino Acids. The thermodynamic studies in this section were motivated by trying to understand the observations that 18-crown-6 (18C6) binds strongly to the protonated side chain of lysine (Lys), however, competitive binding of protonated side chains of arginine (Arg), histidine (His), and especially the N-terminal amino group limit the utility of using 18C6 as a method to identify the number of accessible lysines in a complicated protein.³⁹² Nevertheless, this approach has been

developed into the selective noncovalent adduct protein probing (SNAPP) method for structural elucidation in the gas phase.^{393,394} Thermochemistry relevant to this process has been explored by Rodgers and co-workers using TCID (C) and is summarized in Table 27.^{395–398} This work shows that

Table 27. Bond Dissociation Energies (kJ/mol) at 0 K of (B)H⁺(18C6)^a

B	ref	(B)H ⁺ –18C6	(18C6)H ⁺ –B
CH ₃ NH ₂	C ³⁹⁵	238 (11)	
C ₂ H ₅ NH ₂	C ³⁹⁵	233 (10)	
1-C ₃ H ₇ NH ₂	C ³⁹⁵	224 (9)	
2-C ₃ H ₇ NH ₂	C ³⁹⁵	238 (10)	
1-C ₄ H ₉ NH ₂	C ³⁹⁵	224 (10)	
1,5-NH ₂ -C ₅ H ₁₀ -NH ₂	C ³⁹⁵	186 (10)	
imidazole	C ³⁹⁶	174 (8)	177 (9)
4-CH ₃ -imidazole	C ³⁹⁶	170 (7)	194 (8)
1-CH ₃ -guanidine	C ³⁹⁵	174 (6)	
Gly	C ^{396,397}	223 (10)	262 (10)
Ala	C ^{396,397}	216 (9)	255 (10)
Lys	C ³⁹⁷	168 (7)	
N _α -CH ₃ COLys	C ³⁹⁸	180 (8)	
N _ε -CH ₃ COLys	C ³⁹⁸	172 (6)	
His	C ³⁹⁷	156 (5)	
N _α -CH ₃ COHis	C ³⁹⁸	130 (5)	
Arg	C ³⁹⁷	141 (4)	
N _α -CH ₃ COArg	C ³⁹⁸	137 (5)	

^aUncertainties in parentheses. C = threshold collision-induced dissociation.

protonated amines (mimics of the Lys side chain) bind to 18C6 tightly, comparably to K⁺ (Table 17), whereas the larger imidazole and 4-methylimidazole (mimics of the His side chain) and 1-methylguanidine (mimic of the Arg side chain) bind less tightly (similar to Cs⁺).^{395,396} Protonated glycine (Gly), which can describe interaction of the N-terminus, binds 18C6 only slightly less than the primary amines, but even addition of the small methyl side chain in alanine (Ala) reduces this interaction.³⁹⁶ (Notably this work also provided a more precise determination of the proton affinity of 18C6.³⁹⁶) Comparison of the binding energies of several protonated amino acids to 18C6 shows the order Gly > Ala > Lys > His > Arg.³⁹⁷ Acetylation (Ac = CH₃CO–) of the latter three amino acids at the N-terminus (N_α) shows that the protonated side chain of Lys binds more strongly than those of His and Arg.³⁹⁸ When the side chain of Lys (N_ε) is acetylated, the binding is weaker than to N_α-AcLys, indicating that the protonated side chain is the preferred binding site for 18C6. The preference of 18C6 to bind to protonated primary amines can be largely attributed to the size and shape of the crown ether such that selective binding to the side chains of other basic amino acids can likely be achieved with other appropriately designed crownlike macrocycles.

III.F.6.b. Protonated Nucleobase Pairs. TCID studies of the protonated base pairs of cytosine and its variants have been reported,^{399–403} with values listed in Table 28. It can be seen that the effects are subtle, with all base pairing energies (BPEs) within a range of 20 kJ/mol. Intriguingly, for the homodimers where both nucleobases are the same, methylation at C5 is the only substitution that enhances the BPE. Moving to the nucleoside, in which the sugar is attached to the nucleobase, the BPE lowers appreciably, with intermediate decreases found for

Table 28. Base-Pairing Energies (kJ/mol) of Protonated Nucleobase and Nucleoside Base Pairs at 0 K^a

protonated base pair, (x ¹ C)H ⁺ (y ¹ C)	ref	base pairing energy	
		(x ¹ C)H ⁺ –(y ¹ C)	(x ¹ C)–H ⁺ (y ¹ C)
(C)H ⁺ (C)	C ³⁹⁹	170 (5)	
(m ¹ C)H ⁺ (m ¹ C)	C ⁴⁰¹	171 (5)	
(m ⁵ C)H ⁺ (m ⁵ C)	C ³⁹⁹	177 (5)	
(f ¹ C)H ⁺ (f ¹ C)	C ³⁹⁹	167 (4)	
(br ⁵ C)H ⁺ (br ⁵ C)	C ³⁹⁹	168 (5)	
(i ⁵ C)H ⁺ (i ⁵ C)	C ³⁹⁹	163 (5)	
(m ₂ ^{1,5} C)H ⁺ (m ₂ ^{1,5} C)	C ⁴⁰¹	172 (6)	
(m ¹ f ⁵ C)H ⁺ (m ¹ f ⁵ C)	C ⁴⁰²	166 (5)	
(m ¹ br ⁵ C)H ⁺ (m ¹ br ⁵ C)	C ⁴⁰²	165 (5)	
(dCyd)H ⁺ (dCyd)	C ⁴⁰³	160 (5)	
(m ⁵ dCyd)H ⁺ (m ⁵ dCyd)	C ⁴⁰³	162 (6)	
(m ¹ C)H ⁺ (C)	C ⁴⁰¹	167 (5)	181 (5)
(m ⁵ C)H ⁺ (C)	C ⁴⁰⁰	164 (5)	180 (5)
(C)H ⁺ (f ⁵ C)	C ⁴⁰⁰	157 (5)	180 (5)
(C)H ⁺ (br ⁵ C)	C ⁴⁰⁰	166 (4)	184 (4)
(C)H ⁺ (i ⁵ C)	C ⁴⁰⁰	168 (4)	178 (4)
(m ₂ ^{1,5} C)H ⁺ (C)	C ⁴⁰¹	163 (5)	191 (5)
(m ¹ f ⁵ C)H ⁺ (C)	C ⁴⁰²	167 (5)	173 (5)
(m ¹ br ⁵ C)H ⁺ (C)	C ⁴⁰²	167 (5)	174 (5)
(m ⁵ C)H ⁺ (m ¹ C)	C ⁴⁰¹	170 (5)	173 (5)
(m ¹ C)H ⁺ (m ₂ ^{1,5} C)	C ⁴⁰¹	161 (5)	174 (4)
(m ⁵ C)H ⁺ (m ₂ ^{1,5} C)	C ⁴⁰¹	164 (5)	182 (4)
(m ⁵ dCyd)H ⁺ (dCyd)	C ⁴⁰³	163 (6)	169 (7)

^aValues at 0 K. Uncertainties in parentheses. C = cytosine, dCyd = 2'-deoxycytidine, m = methyl, f = fluorine, br = bromine, i = iodine; superscripts indicate the position of substitution. All values obtained from threshold collision-induced dissociation (C).

halogenation. In the heterodimers, all but one value are lower than for (C)H⁺(C). Notably, these studies yield thermochemistry associated with dissociation to both (xC)H⁺ + (yC) and (xC) + H⁺(yC) fragments such that the difference between the two BPEs is equivalent to the difference in proton affinity of (xC) and (yC). Notably the binding in all of these protonated nucleobase pairs is much stronger than canonical Watson–Crick base pairing, consistent with the enhancement in the strength of interaction associated with the ion-dipole and ion-induced dipole contributions to the binding, as discussed above.

IV. CONCLUSIONS

The strong electrostatic component introduced to noncovalent interactions by the presence of charge manifests itself throughout the thermochemistry reviewed here. The strength of these interactions covers a very broad range, from about 1 (Table 1) to nearly 400 kJ/mol (Table 15). The variations in these values depend critically on both the character of the ion and its ligand. For metal cations, values depend on the charge, size, electronic state, and ability to hybridize (both s–p and s–d hybridization), which leads to interesting periodic trends. For the ligand, their polarizability, dipole and quadrupole moments, rigidity/flexibility, ability to accept or donate π -electrons, and the extent to which the electron density delocalizes all contribute to the range of values observed. Although the addition of sequential ligands generally decreases the bond dissociation energies, a consequence of increasing donation of electron density to the positive charge coupled with steric interactions between ligands, other factors (e.g., hybridization and electronic state) can change this simple expectation. Most of these trends are illustrated in the figures above but also pervade all the thermochemistry tabulated here.

We anticipate that this compendium of evaluated thermodynamic information will be a resource for the community, permitting ready access to a wide range of interesting thermochemistry. The authors believe that citation of any numbers from this work should include the original publication as well, recognizing the effort taken in the actual measurement. In compiling this work, it became clear that the overview allowed us to recognize systems where reanchoring relative scales was needed. It is equally clear that we did not have the time or resources to identify all systems where this could profitably be applied. It is hoped that our overview of the trends in these many numbers will be equally useful, but the reader is reminded that more comprehensive examinations of many of these trends can be found in the original literature.

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Notes

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Biographies

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Peter B. Armentrout received his B.S. degree with highest honors in 1975 from Case Western Reserve University, Cleveland, OH, and a Ph.D. from the California Institute of Technology in 1980, working with Prof. Jesse L. (Jack) Beauchamp. After a postdoctoral appointment at Bell Laboratories in Murray Hill, NJ, with Dr. Robert S. Freund, he was appointed assistant professor at the University of California at Berkeley in 1981. There, he initiated a program that has come to study a wide spectrum of chemistries using guided ion-beam tandem mass spectrometry. In 1987, he joined the faculty at the University of Utah as an associate professor. In 1989, he was promoted to professor, to distinguished professor in 1998, and named Cannon Fellow in 2003. He has received the Biemann Medal from the American Society of Mass Spectrometry in 2001, the Field and Franklin Award for Outstanding Achievement in Mass Spectrometry from the American Chemical Society in 2009, the Utah Governor's Medal for Science and Technology in 2010, and the Rosenblatt Prize for Excellence from the University of Utah in 2011.

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REFERENCES

- (1) Müller-Dethlefs, K.; Hobza, P. Noncovalent Interactions: A Challenge for Experiment and Theory. *Chem. Rev.* **2000**, *100*, 143–167.
- (2) Hobza, P.; Müller-Dethlefs, K. *Non-covalent Interactions: Theory and Experiment*; Royal Society of Chemistry: Cambridge, U.K., 2010.
- (3) Rannulu, N. S.; Rodgers, M. T. Noncovalent Interactions of Cu⁺ with N-Donor Ligands (Pyridine, 4,4'-Dipyridyl, 2,2'-Dipyridyl, and 1,10-Phenanthroline): Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2007**, *111*, 3465–3479.
- (4) Rannulu, N. S.; Rodgers, M. T. Noncovalent Interactions of Zn⁺ with N-Donor Ligands (Pyridine, 4,4'-Dipyridyl, 2,2'-Dipyridyl, and 1,10-Phenanthroline): Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2012**, *116*, 1319–1332.
- (5) Keese, R. G.; Castleman, A. W., Jr. Thermochemical Data on Gas-Phase Ion–Molecule Association and Clustering Reactions. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011–1071.
- (6) Dougherty, D. A. Cation- π Interactions in Chemistry and Biology: An New View of Benzene, Phe, Thr, and Trp. *Science* **1996**, *271*, 163–168.
- (7) Ma, J. C.; Dougherty, D. A. The Cation- π Interaction. *Chem. Rev.* **1997**, *97*, 1303–1324.
- (8) Meot-Ner (Mautner), M. The Ionic Hydrogen Bond. *Chem. Rev.* **2005**, *105*, 213–284.
- (9) Rodgers, M. T.; Armentrout, P. B. Noncovalent Metal-Ligand Bond Energies as Studied by Threshold Collision-Induced Dissociation. *Mass Spectrom. Rev.* **2000**, *19*, 215–247.
- (10) Armentrout, P. B.; Kickel, B. L. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, 1996.
- (11) Rodgers, M. T.; Armentrout, P. B. A Thermodynamic "Vocabulary" for Metal Ion Interactions in Biological Systems. *Acc. Chem. Res.* **2004**, *37*, 989–998.
- (12) Burk, P.; Koppel, I. A.; Koppel, I.; Kurg, R.; Gal, J.-F.; Maria, P.-C.; Herreros, M.; Notario, R.; Abboud, J.-L. M.; Anvia, F.; Taft, R. W.

Revised and Expanded Scale of Gas-Phase Lithium Cation Basicities. An Experimental and Theoretical Study. *J. Phys. Chem. A* **2000**, *104*, 2824–2833.

(13) Mayeux, C.; Burk, P.; Gal, J.-F.; Kaljurand, I.; Koppel, I.; Leito, I.; Sikk, L. Gas-Phase Lithium Cation Basicity: Revisiting the High Basicity Range by Experiment and Theory. *J. Am. Soc. Mass Spectrom.* **2014**, *25*, 1962–1973.

(14) Gal, J.-F.; Maria, P.-C.; Massi, L.; Mayeux, C.; Burk, P.; Tammiku-Taul, J. Cesium Cation Affinities and Basicities. *Int. J. Mass Spectrom.* **2007**, *267*, 7–23.

(15) Gal, J.-F.; Yáñez, M.; Mó, O. Aluminum monocation basicity and affinity scales. *Eur. Mass Spectrom.* **2015**, *21*, 517–532.

(16) Laurence, C.; Gal, J.-F. *Lewis Basicity and Affinity Scales: Data and Measurement*; Wiley: Chichester, U.K., 2010.

(17) Schalley, C. A.; Springer, A. *Mass Spectrometry and Gas-Phase Chemistry of Non-Covalent Complexes*; Wiley: Hoboken, NJ, 2009.

(18) Hunter, E. P. L.; Lias, S. G. Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413–656.

(19) Giese, M.; Albrecht, M.; Rissanen, K. Anion– π Interactions with Fluoroarenes. *Chem. Rev.* **2015**, *115*, 8867–8895.

(20) Ervin, K. M. Experimental Techniques in Gas-Phase Ion Thermochemistry. *Chem. Rev.* **2001**, *101*, 391–444.

(21) Dunbar, R. C. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(22) Price, W. D.; Schnier, P. D.; Williams, E. R. Tandem Mass Spectrometry of Large Biomolecule Ions by Blackbody Infrared Radiative Dissociation. *Anal. Chem.* **1996**, *68*, 859–866.

(23) Dunbar, R. C.; McMahon, T. B.; Thoelmann, D.; Tonner, D. S.; Salahub, D. R.; Wei, D. Zero-Pressure Thermal-Radiation-Induced Dissociation of Gas-Phase Cluster Ions: Comparison of Theory and Experiment for $(\text{H}_2\text{O})_2\text{Cl}^-$ and $(\text{H}_2\text{O})_3\text{Cl}^-$. *J. Am. Chem. Soc.* **1995**, *117*, 12819–12825.

(24) Dunbar, R. C. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(25) Armentrout, P. B. Not Just a Structural Tool: The Use of Guided Ion Beam Tandem Mass Spectrometry to Determine Thermochemistry. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 419–434.

(26) Armentrout, P. B. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(27) Ervin, K. M.; Armentrout, P. B. Translational Energy Dependence of $\text{Ar}^+ + \text{XY} \rightarrow \text{ArX}^+ + \text{Y}$ ($\text{XY} = \text{H}_2, \text{D}_2, \text{HD}$) from Thermal to 30 eV c.m. *J. Chem. Phys.* **1985**, *83*, 166–189.

(28) Rodgers, M. T. Substituent Effects in the Binding of Alkali Metal Ions to Pyridines Studied by Threshold Collision-Induced Dissociation and Ab Initio Theory: The Methylpyridines. *J. Phys. Chem. A* **2001**, *105*, 2374–2383.

(29) Armentrout, P. B.; Simons, J. Understanding Heterolytic Bond Cleavage. *J. Am. Chem. Soc.* **1992**, *114*, 8627–8633.

(30) Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. Sequential Bond Energies of $\text{Fe}(\text{CO})_x^+$ ($x = 1 - 5$): Systematic Effects on Collision-Induced Dissociation Measurements. *J. Am. Chem. Soc.* **1991**, *113*, 8590–8601.

(31) Muntean, F.; Armentrout, P. B. Guided Ion Beam Study of Collision-Induced Dissociation Dynamics: Integral and Differential Cross Sections. *J. Chem. Phys.* **2001**, *115*, 1213–1228.

(32) Hales, D. A.; Lian, L.; Armentrout, P. B. Collision-Induced Dissociation of Nb_n^+ ($n = 2 - 11$): Bond Energies and Dissociation Pathways. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 269–301.

(33) Rodgers, M. T.; Ervin, K. M.; Armentrout, P. B. Statistical Modeling of Collision-Induced Dissociation Thresholds. *J. Chem. Phys.* **1997**, *106*, 4499–4508.

(34) Rodgers, M. T.; Armentrout, P. B. Statistical Modeling of Competitive Threshold Collision-Induced Dissociation. *J. Chem. Phys.* **1998**, *109*, 1787–1800.

(35) Armentrout, P. B. Statistical modeling of sequential collision-induced dissociation. *J. Chem. Phys.* **2007**, *126*, 234302.

(36) Armentrout, P. B.; Ervin, K. M.; Rodgers, M. T. Statistical Rate Theory and Kinetic Energy-Resolved Ion Chemistry – Theory and Applications. *J. Phys. Chem. A* **2008**, *112*, 10071–10085.

(37) Dalleska, N. F.; Honma, K.; Armentrout, P. B. Stepwise Solvation Enthalpies of Protonated Water Clusters: Collision Induced Dissociation as an Alternative to Equilibrium Studies. *J. Am. Chem. Soc.* **1993**, *115*, 12125–12131.

(38) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. Solvation of Transition Metal Ions by Water. Sequential Binding Energies of $\text{M}^+(\text{H}_2\text{O})_x$ ($x = 1 - 4$) for $\text{M} = \text{Ti} - \text{Cu}$ Determined by Collision-Induced Dissociation. *J. Am. Chem. Soc.* **1994**, *116*, 3519–3528.

(39) Dalleska, N. F.; Tjelta, B. L.; Armentrout, P. B. Sequential Bond Energies of Water to Na^+ ($3s^0$), Mg^+ ($3s^1$), and Al^+ ($3s^2$). *J. Phys. Chem.* **1994**, *98*, 4191–4195.

(40) Rodgers, M. T.; Armentrout, P. B. Collision-Induced Dissociation Measurements on $\text{Li}^+(\text{H}_2\text{O})_n$, $n = 1 - 6$: The First Direct Measurement of the $\text{Li}^+\text{-OH}_2$ Bond Energy. *J. Phys. Chem. A* **1997**, *101*, 1238–1249.

(41) Rodgers, M. T.; Armentrout, P. B. Absolute Binding Energies of Lithium Ions to Short Chain Alcohols, $\text{C}_n\text{H}_{n+2}\text{O}$, $n = 1 - 4$, Determined by Threshold Collision-Induced Dissociation. *J. Phys. Chem. A* **1997**, *101*, 2614–2625.

(42) Iceman, C.; Armentrout, P. B. Collision-Induced Dissociation and Theoretical Studies of K^+ Complexes with Ammonia: A Test of Theory for Potassium Ions. *Int. J. Mass Spectrom.* **2003**, *222*, 329–349.

(43) Amicangelo, J. C.; Armentrout, P. B. Ligand exchange reactions of sodium cation complexes examined using guided ion beam mass spectrometry: Relative and absolute dissociation free energies and entropies. *J. Phys. Chem. A* **2004**, *108*, 10698–10713.

(44) van Koppen, P. A. M.; Bowers, M. T.; Beauchamp, J. L.; Dearden, D. V. Organometallic Reaction Energetics from Product Kinetic Energy Release Distributions. *ACS Symp. Series* **1990**, *428*, 34–54.

(45) Kebarle, P. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(46) Kellersberger, K. A.; Dearden, D. V. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(47) Baer, T. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(48) McLuckey, S. A.; Cameron, D.; Cooks, R. G. Proton Affinities from Dissociations of Proton-Bound Dimers. *J. Am. Chem. Soc.* **1981**, *103*, 1313–1317.

(49) Cooks, R. G.; Wong, P. H. Kinetic Method of Making Thermochemical Determinations: Advances and Applications. *Acc. Chem. Res.* **1998**, *31*, 379–386.

(50) Zheng, X.; Cooks, R. G.; Augusti, R.; Tao, W. A. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.

(51) Cheng, X.; Wu, Z.; Fenselau, C. Collision Energy Dependence of Proton-bound Dimer Dissociation: Entropy Effects, Proton Affinities, and Intramolecular Hydrogen-bonding in Protonated Peptides. *J. Am. Chem. Soc.* **1993**, *115*, 4844–4848.

(52) Armentrout, P. B. Entropy Measurements and the Kinetic Method: A Statistically Meaningful Approach. *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 371–379.

(53) Armentrout, P. B. Is the Kinetic Method a Thermodynamic Method? *J. Mass Spectrom.* **1999**, *34*, 74–78.

(54) Drahos, L.; Vekey, K. How Closely Related are the Effective and Real Temperature. *J. Mass Spectrom.* **1999**, *34*, 79–84.

(55) Cooks, R. G.; Koskinen, J. T.; Thomas, P. D. The Kinetic Method of Making Thermochemical Determinations. *J. Mass Spectrom.* **1999**, *34*, 85–92.

(56) Ervin, K. M. Microcanonical Analysis of the Kinetic Method: The Meaning of the “Apparent Entropy”. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 435–452.

- (57) Lee, S.; Wyttenbach, T.; Bowers, M. T. Gas phase structures of sodiated oligosaccharides by ion mobility/ion chromatography methods. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167–168*, 605–614.
- (58) Hoaglund, C. S.; Valentine, S. J.; Clemmer, D. E. An Ion Trap Interface for ESI-Ion Mobility Experiments. *Anal. Chem.* **1997**, *69*, 4156–4161.
- (59) Kanu, A. B.; Dwivedi, P.; Tam, M.; Matz, L.; Hill, H. H. "Ion Mobility-Mass Spectrometry. *J. Mass Spectrom.* **2008**, *43*, 1–22.
- (60) Viehland, L. A. Interaction Potentials for the Alkali Ion - Rare-Gas Systems. *Chem. Phys.* **1984**, *85*, 291–305.
- (61) Mason, E. A.; Schamp, H. W. Mobility of gaseous ions in weak electric fields. *Ann. Phys.* **1958**, *4*, 233–270.
- (62) Milloy, H. B.; Watts, R. O.; Robson, R. E.; Elford, M. T. The Determination of Ion-Atom Interaction Potentials. *Aust. J. Phys.* **1974**, *27*, 787–794.
- (63) Dunbar, R. C. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.
- (64) Bartmess, J. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.
- (65) Cross, R. J. Determination of intermolecular potentials using high-energy molecular beams. *Acc. Chem. Res.* **1975**, *8*, 225–230.
- (66) Budenholzer, F. E.; Gislason, E. A.; Jorgensen, A. D. Comment on "Recent determinations of potassium ion-rare gas potentials". *J. Chem. Phys.* **1983**, *78*, 5279–5280.
- (67) Armentrout, P. B. In *Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1.
- (68) Armentrout, P. B. The Power of Accurate Energetics (or Thermochemistry: What is it Good for?). *J. Am. Soc. Mass Spectrom.* **2013**, *24*, 173–185.
- (69) Takebe, M. The generalized mobility curve for alkali ions in rare gases: Clustering reactions and mobility curves. *J. Chem. Phys.* **1983**, *78*, 7223–7226.
- (70) Gatland, I. R.; Lamm, D. R.; Thackston, M. G.; Pope, W. M.; Eisele, F. L.; Ellis, H. W.; McDaniel, E. W. Mobilities and interaction potentials for $\text{Rb}^+ - \text{Ar}$, $\text{Rb}^+ - \text{Kr}$, and $\text{Rb}^+ - \text{Xe}$. *J. Chem. Phys.* **1978**, *69*, 4951–4954.
- (71) Gatland, I. R.; Thackston, M. G.; Pope, W. M.; Eisele, F. L.; Ellis, H. W.; McDaniel, E. W. Mobilities and interaction potentials for $\text{Cs}^+ - \text{Ar}$, $\text{Cs}^+ - \text{Kr}$, and $\text{Cs}^+ - \text{Xe}$. *J. Chem. Phys.* **1978**, *68*, 2775–2778.
- (72) Gatland, I. R. Ion mobility test of $\text{Li}^+ - \text{Ar}$ potentials. *J. Chem. Phys.* **1981**, *75*, 4162–4163.
- (73) Lamm, D. R.; Thackston, M. G.; Eisele, F. L.; Ellis, H. W.; Twist, J. R.; Pope, W. M.; Gatland, I. R.; McDaniel, E. W. Mobilities and interaction potentials for $\text{K}^+ - \text{Ar}$, $\text{K}^+ - \text{Kr}$, and $\text{K}^+ - \text{Xe}$. *J. Chem. Phys.* **1981**, *74*, 3042–3045.
- (74) Rajan, M. S.; Gislason, E. A. Determination of cesium ion-rare gas potentials from total cross section measurements. *J. Chem. Phys.* **1983**, *78*, 2428–2437.
- (75) Powers, T. R.; Cross, R. J. Molecular beam determination of alkali ion-rare gas potentials. *J. Chem. Phys.* **1973**, *58*, 626–633.
- (76) Polak-Dingels, P.; Rajan, M. S.; Gislason, E. A. Determination of lithium ion-rare gas potentials from total cross section measurements. *J. Chem. Phys.* **1982**, *77*, 3983–3993.
- (77) Kemper, P. R.; Hsu, M.-T.; Bowers, M. T. Transition-Metal Ion - Rare Gas Clusters: Bond Strengths and Molecular Parameters for $\text{Co}^+(\text{He/Ne})_n$, $\text{Ni}^+(\text{He/Ne})_n$, and $\text{Cr}^+(\text{He/Ne/Ar})$. *J. Phys. Chem.* **1991**, *95*, 10600–10609.
- (78) Walter, D.; Sievers, M. R.; Armentrout, P. B. Alkali Ion Carbonyls: Sequential Bond Energies of $\text{Li}^+(\text{CO})_x$ ($x = 1 - 3$), $\text{Na}^+(\text{CO})_x$ ($x = 1, 2$), and $\text{K}^+(\text{CO})$. *Int. J. Mass Spectrom. Ion Processes* **1998**, *175*, 93–106.
- (79) Tjelta, B. L.; Walter, D.; Armentrout, P. B. Determination of Weak $\text{Fe}^+ - \text{L}$ Bond Energies ($\text{L} = \text{Ar}, \text{Kr}, \text{Xe}, \text{N}_2, \text{CO}_2$) by Ligand Exchange Reactions and Collision-Induced Dissociation. *Int. J. Mass Spectrom.* **2001**, *204*, 7–21.
- (80) Koszinowski, K.; Schröder, D.; Schwarz, H.; Holthausen, M. C.; Sauer, J.; Koizumi, H.; Armentrout, P. B. Bond Dissociation Energies and Structures of CuNO^+ and $\text{Cu}(\text{NO})_2^+$. *Inorg. Chem.* **2002**, *41*, 5882–5890; *Inorg. Chem.* **2002**, *41*, 7170.
- (81) Andersen, A.; Muntean, F.; Walter, D.; Rue, C.; Armentrout, P. B. Collision-Induced Dissociation and Theoretical Studies of Mg^+ Complexes with CO , CO_2 , NH_3 , CH_4 , CH_3OH , and C_6H_6 . *J. Phys. Chem. A* **2000**, *104*, 692–705.
- (82) Haynes, C. L.; Armentrout, P. B.; Perry, J. K.; Goddard, W. A., III Experimental and Theoretical Studies of $\text{Co}(\text{CH}_4)_x^+$ with $x = 1 - 4$. *J. Phys. Chem.* **1995**, *99*, 6340–6346.
- (83) Tjelta, B. L.; Armentrout, P. B. Gas-Phase Metal Ion Ligation: Collision-Induced Dissociation of $\text{Fe}(\text{N}_2)_x^+$ ($x = 1 - 5$) and $\text{Fe}(\text{CH}_2\text{O})_x^+$ ($x = 1 - 4$). *J. Phys. Chem. A* **1997**, *101*, 2064–2073.
- (84) Pilgrim, J. S.; Yeh, C. S.; Berry, K. R.; Duncan, M. A. Photodissociation Spectroscopy of Mg^+ -rare Gas Complexes. *J. Chem. Phys.* **1994**, *100*, 7945–7956.
- (85) Heidecke, S. A.; Fu, Z.; Colt, J. R.; Morse, M. D. Spectroscopy of AlAr and AlKr from 31 000 cm^{-1} to the ionization limit. *J. Chem. Phys.* **1992**, *97*, 1692–1710.
- (86) Meot-Ner, M. M.; Lias, S. G. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD. <http://webbook.nist.gov> (retrieved Oct 6, 2015).
- (87) Zhang, X.-G.; Armentrout, P. B. Sequential Bond Energies of $\text{Pt}(\text{CO})_x^+$ ($x = 1 - 4$) Determined by Collision Induced Dissociation. *Organometallics* **2001**, *20*, 4266–4273.
- (88) Rothe, E. W.; Bernstein, R. B. Total collision cross sections for the interactions of atomic beams of alkali metals with gases. *J. Chem. Phys.* **1959**, *31*, 1619–1627.
- (89) Wilson, R. G.; Brewer, G. R. *Ion Beams with Applications to Ion Implantation*; Wiley: New York, 1973.
- (90) Bushnell, J. E.; Kemper, P. R.; Bowers, M. T. $\text{Na}^+/\text{K}^+(\text{H}_2)_{1,2}$ Clusters: Binding Energies from Theory and Experiment. *J. Phys. Chem.* **1994**, *98*, 2044–2049.
- (91) Kemper, P. R.; Bushnell, J.; Bowers, M. T.; Gellene, G. I. Binding between Ground-State Aluminum Ions and Small Molecules: $\text{Al}^+ \bullet (\text{H}_2/\text{CH}_4/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6)_n$. Can Al^+ Insert into H_2 ? *J. Phys. Chem. A* **1998**, *102*, 8590–8597.
- (92) Bushnell, J. E.; Kemper, P. R.; Maitre, P.; Bowers, M. T. Insertion of Sc^+ into H_2 : The First Example of Cluster-Mediated σ -Bond Activation by a Transition Metal Center. *J. Am. Chem. Soc.* **1994**, *116*, 9710–9718.
- (93) Bushnell, J. E.; Maitre, P.; Kemper, P. R.; Bowers, M. T. Binding Energies of $\text{Ti}^+(\text{H}_2)_{1-6}$ Clusters: Theory and Experiment. *J. Chem. Phys.* **1997**, *106*, 10153–10167.
- (94) Bushnell, J. E.; Kemper, P. R.; Bowers, M. T. Spin Change Induced in Vanadium(I) by Low-Field Ligands: Binding Energies of $\text{V}^+(\text{H}_2)_n$ Cluster ($n = 1-7$). *J. Phys. Chem.* **1993**, *97*, 11628–11634.
- (95) Kemper, P. R.; Weis, P.; Bowers, M. T. $\text{Cr}^+(\text{H}_2)_n$ Clusters: Asymmetric Bonding from a Symmetric Ion. *Int. J. Mass Spectrom. Ion Processes* **1997**, *160*, 17–37.
- (96) Weis, P.; Kemper, P. R.; Bowers, M. T. $\text{Mn}^+(\text{H}_2)_n$ and $\text{Zn}^+(\text{H}_2)_n$ Clusters: Influence of 3d and 4s Orbitals on Metal-Ligand Bonding. *J. Phys. Chem. A* **1997**, *101*, 2809–2816.
- (97) Bushnell, J. E.; Kemper, P. R.; Bowers, M. T. Factors affecting σ bond activation in simple systems: Measurement of experimental binding energies of $\text{Fe}^+(\text{H}_2)_{1-6}$ clusters. *J. Phys. Chem.* **1995**, *99*, 15602–15607.
- (98) Kemper, P. R.; Bushnell, J.; von Helden, G.; Bowers, M. T. $\text{Co}^+(\text{H}_2)_n$ Clusters: Binding Energies and Molecular Parameters. *J. Phys. Chem.* **1993**, *97*, 52–58.
- (99) Kemper, P. R.; Weis, P.; Bowers, M. T. $\text{Ni}^+(\text{H}_2)_n$: Ligand Bond Energies for Ground State Ions. *Chem. Phys. Lett.* **1998**, *293*, 503–510.
- (100) Kemper, P. R.; Weis, P.; Bowers, M. T.; Maitre, P. Origin of Bonding Interactions in $\text{Cu}^+(\text{H}_2)_n$ Clusters: An Experimental and Theoretical Investigation. *J. Am. Chem. Soc.* **1998**, *120*, 13494–13502.
- (101) Bushnell, J. E.; Kemper, P. R.; van Koppen, P.; Bowers, M. T. Mechanistic and Energetic Details of Adduct Formation and σ -Bond Activation in $\text{Zr}^+(\text{H}_2)_n$ Clusters. *J. Phys. Chem. A* **2001**, *105*, 2216–2224.
- (102) Wu, C. H. Binding energies of LiH_2 and LiH_2^+ and the ionization potential of LiH_2 . *J. Chem. Phys.* **1979**, *71*, 783–787.

- (103) Haynes, C. L.; Armentrout, P. B. Guided Ion-Beam Determination of the $\text{Co}^+\text{-H}_2$ Bond Dissociation Energy. *Chem. Phys. Lett.* **1996**, 249, 64–70.
- (104) Walter, D.; Armentrout, P. B. Sequential Bond Dissociation Energies of $\text{M}^+(\text{NH}_3)_x$ ($x = 1 - 4$) for $\text{M} = \text{Ti} - \text{Cu}$. *J. Am. Chem. Soc.* **1998**, 120, 3176–3187.
- (105) Liyanage, R.; Styles, M. L.; O'Hair, R. A. J.; Armentrout, P. B. Sequential Bond Energies of $\text{Pt}^+(\text{NH}_3)_x$ ($x = 1 - 4$) Determined by Collision-Induced Dissociation and Theory. *Int. J. Mass Spectrom.* **2003**, 227, 47–62.
- (106) Marinelli, P. J.; Squires, R. R. Sequential Solvation of Atomic Transition-Metal Ions. The Second Solvent Molecule Can Bind More Strongly Than the First. *J. Am. Chem. Soc.* **1989**, 111, 4101–4103.
- (107) Amicangelo, J. C.; Armentrout, P. B. Relative and Absolute Bond Dissociation Energies of Sodium Cation Complexes Determined Using Competitive Collision-Induced Dissociation Experiments. *Int. J. Mass Spectrom.* **2001**, 212, 301–325.
- (108) El Aribi, H.; Rodriguez, C. F.; Shoeib, T.; Ling, Y.; Hopkinson, A. C.; Siu, K. W. M. Threshold Collision-Induced Dissociation Determination and Molecular Orbital Calculations of the Binding Energies of Sodium and Silver Ions to Small Nitrogen-Containing Ligands. *J. Phys. Chem. A* **2002**, 106, 8798–8805.
- (109) Castleman, A. W., Jr.; Holland, P. M.; Lindsay, D. M.; Peterson, K. A. The Properties of Clusters in the Gas Phase: Ammonia About Metal Ions. *J. Am. Chem. Soc.* **1978**, 100, 6039–6045.
- (110) Castleman, A. W., Jr. The Properties of Clusters in the Gas Phase: Ammonia About Bi^+ , Rb^+ , and K^+ . *Chem. Phys. Lett.* **1978**, 53, 560–564.
- (111) Davidson, W. R.; Kebabian, P. Binding energies and stabilities of potassium ion complexes from studies of the gas phase ion equilibria $\text{K}^+ + \text{M} = \text{K}^+\text{M}$. *J. Am. Chem. Soc.* **1976**, 98, 6133–6138.
- (112) Holland, P. M.; Castleman, A. W. The thermochemical properties of gas-phase transition metal ion complexes. *J. Chem. Phys.* **1982**, 76, 4195–4205.
- (113) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumi, G.; Vasanwala, R.; Yazdani, S. Free Energies of Cation-molecule Complex Formation and of Cation-solvent Transfers. *Pure Appl. Chem.* **1990**, 62, 17–23.
- (114) Woodin, R. L.; Beauchamp, J. L. Binding of Li^+ to Lewis bases in the gas phase. Reversals in methyl substituent effects for different reference acids. *J. Am. Chem. Soc.* **1978**, 100, 501–508.
- (115) Hoyau, S.; Norrman, K.; McMahon, T. B.; Ohanessian, G. A Quantitative Basis for a Scale of Na^+ Affinities of Organic and Small Biological Molecules in the Gas Phase. *J. Am. Chem. Soc.* **1999**, 121, 8864–8875.
- (116) McMahon, T. B.; Ohanessian, G. An Experimental and Ab Initio Study of the Nature of the Binding in Gas-Phase Complexes of Sodium Ions. *Chem. - Eur. J.* **2000**, 6, 2931–2941.
- (117) Uppal, J. S.; Staley, R. H. Relative Binding Energies of Organic Molecules to Mn^+ in the Gas Phase. *J. Am. Chem. Soc.* **1982**, 104, 1238–1243.
- (118) Armentrout, P. B.; Rodgers, M. T. An Absolute Sodium Cation Affinity Scale: Threshold Collision-Induced Dissociation Experiments and ab Initio Theory. *J. Phys. Chem. A* **2000**, 104, 2238–2247.
- (119) Gilligan, J. J.; McCunn, L. R.; Leskiw, B. D.; Herman, Z.; Castleman, A. W. Associative ionization of excited sodium species with various ligands: assessing relative bonding strengths of ion-ligand interactions. *Int. J. Mass Spectrom.* **2001**, 204, 247–253.
- (120) Meyer, F.; Armentrout, P. B. Sequential Bond Energies of $\text{Ti}(\text{CO})_x^+$, $x = 1 - 7$. *Mol. Phys.* **1996**, 88, 187–197.
- (121) Sievers, M. R.; Armentrout, P. B. Collision-Induced Dissociation Studies of $\text{V}(\text{CO})_x^+$, $x = 1 - 7$: Sequential Bond Energies and the Heat of Formation of $\text{V}(\text{CO})_6$. *J. Phys. Chem.* **1995**, 99, 8135–8141.
- (122) Khan, F. A.; Clemmer, D. E.; Schultz, R. H.; Armentrout, P. B. Sequential Bond Energies of $\text{Cr}(\text{CO})_x^+$, $x = 1 - 6$. *J. Phys. Chem.* **1993**, 97, 7978–7987.
- (123) Armentrout, P. B. Building organometallic complexes from the bare metal: Thermochemistry and electronic structure along the way. *Acc. Chem. Res.* **1995**, 28, 430–436.
- (124) Goebel, S.; Haynes, C. L.; Khan, F. A.; Armentrout, P. B. Collision-Induced Dissociation Studies of $\text{Co}(\text{CO})_x^+$, $x = 1 - 5$: Sequential Bond Energies and the Heat of Formation of $\text{Co}(\text{CO})_4$. *J. Am. Chem. Soc.* **1995**, 117, 6994–7002.
- (125) Carpenter, C. J.; van Koppen, P. A. M.; Bowers, M. T. Details of Potential Energy Surfaces Involving C-C Bond Activation: Reactions of Fe^+ , Co^+ , and Ni^+ with Acetone. *J. Am. Chem. Soc.* **1995**, 117, 10976–10985.
- (126) Khan, F. A.; Steele, D. L.; Armentrout, P. B. Ligand Effects in Organometallic Thermochemistry: The Sequential Bond Energies of $\text{Ni}(\text{CO})_x^+$, $\text{Ni}(\text{N}_2)_x^+$ ($x = 1 - 4$) and $\text{Ni}(\text{NO})_x^+$ ($x = 1 - 3$). *J. Phys. Chem.* **1995**, 99, 7819–7828.
- (127) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. Sequential Bond Energies of $\text{Cu}(\text{CO})_x^+$ and $\text{Ag}(\text{CO})_x^+$ ($x = 1 - 4$). *J. Am. Chem. Soc.* **1995**, 117, 4071–4081.
- (128) Castleman, A. W., Jr.; Peterson, K. I.; Upschulte, B. L.; Schelling, F. J. Energetics and Structures of Na^+ Cluster Ions. *Int. J. Mass Spectrom. Ion Phys.* **1983**, 47, 203–206.
- (129) Distefano, G. Photoionization Study of $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$. *J. Res. Natl. Bur. Stand., Sect. A* **1970**, 74A, 233–239.
- (130) Norwood, K.; Ali, A.; Flesch, G. D.; Ng, C. Y. A photoelectron-photoion coincidence study of iron pentacarbonyl. *J. Am. Chem. Soc.* **1990**, 112, 7502–7508.
- (131) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. Theoretical studies of the first- and second-row transition-metal mono- and dicarbonyl positive ions. *J. Chem. Phys.* **1990**, 93, 609–624.
- (132) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. Ion beam studies of the reactions of Group VIII metal ions with alkanes: correlation of thermochemical properties and reactivity. *Organometallics* **1982**, 1, 963–968.
- (133) Schröder, D.; Schwarz, H. Ligand effects as probes for mechanistic aspects of remote C-H bond activation by Iron(I) cations in the gas phase. *J. Organomet. Chem.* **1995**, 504, 123–135.
- (134) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Van Koppen, P.; Bowers, M. T. Kinetic energy release distributions as a probe of transition-metal-mediated hydrogen-hydrogen, carbon-hydrogen, and carbon-carbon bond formation processes: reactions of cobalt and nickel ions with alkanes. *J. Am. Chem. Soc.* **1988**, 110, 1–14.
- (135) Sievers, M. R.; Jarvis, L. M.; Armentrout, P. B. Transition Metal Ethene Bonds: Thermochemistry of $\text{M}^+(\text{C}_2\text{H}_4)_n$ ($\text{M} = \text{Ti} - \text{Cu}$, $n = 1$ and 2) Complexes. *J. Am. Chem. Soc.* **1998**, 120, 1891–1899.
- (136) Sievers, M. R.; Armentrout, P. B. Reactions of CO and CO_2 with Gas Phase Mo^+ , MoO^+ , and MoO_2^+ . *J. Phys. Chem. A* **1998**, 102, 10754–10762.
- (137) Sievers, M. R.; Armentrout, P. B. Gas Phase Activation of Carbon Dioxide by Niobium and Niobium Monoxide Cations. *Int. J. Mass Spectrom.* **1998**, 179–180, 103–115.
- (138) Sievers, M. R.; Armentrout, P. B. Reactions of Y^+ , YO^+ and YO_2^+ with CO and CO_2 . *Inorg. Chem.* **1999**, 38, 397–402.
- (139) Sievers, M. R.; Armentrout, P. B. Oxidation of CO and Reduction of CO_2 by Gas Phase Zr^+ , ZrO^+ , and ZrO_2^+ . *Int. J. Mass Spectrom.* **1999**, 185–187, 117–129.
- (140) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Harvey, J. N.; Schwarz, H. Kinetic-energy dependence of competitive spin-allowed and spin-forbidden reactions: $\text{V}^+ + \text{CS}_2$. *J. Chem. Phys.* **1999**, 110, 7858–7870.
- (141) Schröder, D.; Kretzschmar, I.; Schwarz, H.; Rue, C.; Armentrout, P. B. On the Structural Dichotomy of Cationic, Anionic, and Neutral FeS_2 . *Inorg. Chem.* **1999**, 38, 3474–3480.
- (142) Kretzschmar, I.; Schröder, D.; Schwarz, H.; Rue, C.; Armentrout, P. B. Thermochemistry and Reactivity of Cationic Scandium and Titanium Sulfide in the Gas Phase. *J. Phys. Chem. A* **2000**, 104, 5046–5058.
- (143) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Schwarz, H. Guided Ion Beam Studies of the State-Specific Reactions

of Cr^+ and Mn^+ with CS_2 and COS . *Int. J. Mass Spectrom.* **2001**, 210–211, 283–301.

(144) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Schwarz, H. J. Guided Ion Beam Studies of the Reactions of Fe^+ and Co^+ with CS_2 and COS . *J. Phys. Chem. A* **2001**, 105, 8456–8464.

(145) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Schwarz, H. Guided Ion Beam Studies of the Reactions of Ni^+ , Cu^+ , and Zn^+ with CS_2 and COS . *J. Phys. Chem. A* **2002**, 106, 9788–9797.

(146) Kretzschmar, I.; Schröder, D.; Schwarz, H.; Armentrout, P. B. Structure, Thermochemistry, and Reactivity of MS_n^+ Cations ($\text{M} = \text{V}, \text{Mo}$; $n = 1 - 3$) in the Gas Phase. *Int. J. Mass Spectrom.* **2003**, 228, 439–456.

(147) Kretzschmar, I.; Schröder, D.; Schwarz, H.; Armentrout, P. B. Gas-phase thermochemistry of the early cationic transition-metal sulfides of the second row: YS^+ , ZrS^+ , and NbS^+ . *Int. J. Mass Spectrom.* **2006**, 249–250, 263–278.

(148) Armentrout, P. B.; Kretzschmar, I. Experimental and Theoretical Studies of the Reaction of Rh^+ with CS_2 in the Gas-phase: Thermochemistry of RhS^+ and RhCS^+ . *J. Phys. Chem. A* **2009**, 113, 10955–10965.

(149) Armentrout, P. B.; Kretzschmar, I. Experimental and Theoretical Studies of the Reaction of Pd^+ with CS_2 in the Gas-phase: Thermochemistry of PdS^+ and PdCS^+ . *Inorg. Chem.* **2009**, 48, 10371–10382.

(150) Armentrout, P. B.; Kretzschmar, I. Guided ion beam and theoretical studies of the reaction of Ag^+ with CS_2 : Gas-phase thermochemistry of AgS^+ and AgCS^+ and insight into spin-forbidden reactions. *J. Chem. Phys.* **2010**, 132, 024306–024301–024310.

(151) Armentrout, P. B.; Kretzschmar, I. Guided Ion Beam and Theoretical Studies of the Reaction of Ru^+ with CS_2 in the Gas-phase: Thermochemistry of RuC^+ , RuS^+ , and RuCS^+ . *Phys. Chem. Chem. Phys.* **2010**, 12, 4078–4091.

(152) Dzidic, I.; Kebarle, P. Hydration of the alkali ions in the gas phase. Enthalpies and entropies of reactions $\text{M}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{M}^+(\text{H}_2\text{O})_n$. *J. Phys. Chem.* **1970**, 74, 1466–1474.

(153) Searles, S. K.; Kebarle, P. Hydration of the Potassium Ion in the Gas Phase: Enthalpies and Entropies of Hydration Reactions $\text{K}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{K}^+(\text{H}_2\text{O})_n$ for $n = 1$ to $n = 6$. *Can. J. Chem.* **1969**, 47, 2619–2627.

(154) Ke, H.; van der Linde, C.; Lisy, J. M. Insights into the Structures of the Gas-Phase Hydrated Cations $\text{M}^+(\text{H}_2\text{O})_n\text{Ar}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$, and Cs ; $n = 3 - 5$) Using Infrared Photodissociation Spectroscopy and Thermodynamic Analysis. *J. Phys. Chem. A* **2015**, 119, 2037–2051.

(155) Burdett, N. A.; Hayhurst, A. N. Hydration of Gas-phase Ions and the Measurement of Boundary-layer Cooling during Flame Sampling into a Mass Spectrometer. *J. Chem. Soc., Faraday Trans. 1* **1982**, 78, 2997–3007.

(156) McKnight, L. G.; Sawina, J. M. Drift Velocities and Interactions of Cs^+ Ions with Atmospheric Gases. *J. Chem. Phys.* **1972**, 57, 5156–5162.

(157) Sunner, J.; Kebarle, P. Unimolecular Dissociation of Ions. Effect on Mass-Spectrometric Measurements of Ion–Molecule Association Equilibria. *J. Phys. Chem.* **1981**, 85, 327–335.

(158) Willey, K. F.; Yeh, C. S.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. Photodissociation spectroscopy of $\text{Mg}^+\text{-H}_2\text{O}$ and $\text{Mg}^+\text{-D}_2\text{O}$. *J. Chem. Phys.* **1992**, 97, 8886–8895.

(159) Kochanski, E.; Constantin, E. Theoretical and experimental studies of the system $\text{Ca}^+(\text{H}_2\text{O})_n$ for $n = 1$ to 10. *J. Chem. Phys.* **1987**, 87, 1661–1665.

(160) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. Production of Hydrated Metal Ions by Fast Ion or Atom Beam Sputtering. Collision-Induced Dissociation and Successive Hydration Energies of Gaseous Cu^+ with 1–4 Water Molecules. *J. Am. Chem. Soc.* **1989**, 111, 5036–5043.

(161) Schultz, R. H.; Armentrout, P. B. Gas-Phase Metal Ligation: Collision-induced Dissociation of $\text{Fe}(\text{H}_2\text{O})_x^+$ and $\text{Fe}(\text{CH}_4)_x^+$ ($x = 1 - 4$). *J. Phys. Chem.* **1993**, 97, 596–603.

(162) Sweeney, A. F.; Armentrout, P. B. Guided Ion Beam Studies of the Collision-induced Dissociation of $\text{CuOH}^+(\text{H}_2\text{O})_n$ ($n = 1 - 4$): Comprehensive Thermodynamic Data for Copper Ion Hydration. *J. Phys. Chem. A* **2014**, 118, 10210–10222.

(163) Tang, I. N.; Lian, M. S.; Castleman, A. W., Jr. Mass spectrometric study of gas-phase clustering reactions: Hydration of the monovalent strontium ion. *J. Chem. Phys.* **1976**, 65, 4022–4027.

(164) Tang, N.; Castleman, A. W., Jr. Mass Spectrometric Study of the Gas-Phase Hydration of the Monovalent Lead Ion. *J. Chem. Phys.* **1972**, 57, 3638–3644.

(165) Tang, I. N.; Castleman, A. W., Jr. Mass spectrometric study of gas-phase clustering reactions: Hydration of the monovalent bismuth ion. *J. Chem. Phys.* **1974**, 60, 3981–3986.

(166) Koizumi, H.; Larson, M.; Muntean, F.; Armentrout, P. B. Sequential Bond Energies of $\text{Ag}^+(\text{H}_2\text{O})_n$ and $\text{Ag}^+(\text{dimethyl ether})_n$, $n = 1 - 4$, Determined by Threshold Collision-Induced Dissociation. *Int. J. Mass Spectrom.* **2003**, 228, 221–235.

(167) El Aribi, H.; Shoeib, T.; Ling, Y.; Rodriguez, C. F.; Hopkinson, A. C.; Siu, K. W. M. Binding Energies of the Silver Ion to Small Oxygen-Containing Ligands: Determination by Means of Density Functional Theory and Threshold Collision-Induced Dissociation. *J. Phys. Chem. A* **2002**, 106, 2908–2914.

(168) Bauschlicher, C. W.; Sodupe, M.; Partridge, H. A theoretical study of the positive and dipositive ions of $\text{M}(\text{NH}_3)_n$ and $\text{M}(\text{H}_2\text{O})_n$ for $\text{M} = \text{Mg}, \text{Ca}$, or Sr . *J. Chem. Phys.* **1992**, 96, 4453–4463.

(169) Carl, D. R.; Armentrout, P. B. Threshold Collision-Induced Dissociation of Hydrated Magnesium: Experimental and Theoretical Investigation of the Binding Energies for $\text{Mg}^{2+}(\text{H}_2\text{O})_x$ complexes ($x = 2 - 10$). *ChemPhysChem* **2013**, 14, 681–697.

(170) Carl, D. R.; Moision, R. M.; Armentrout, P. B. Binding Energies for the Inner Hydration Shells of Ca^{2+} : An Experimental and Theoretical Investigation of $\text{Ca}^{2+}(\text{H}_2\text{O})_x$ Complexes ($x = 5 - 9$). *Int. J. Mass Spectrom.* **2007**, 265, 308–325.

(171) Carl, D. R.; Armentrout, P. B. Experimental investigation of the complete inner shell hydration energies of Ca^{2+} : Threshold collision-induced dissociation of $\text{Ca}^{2+}(\text{H}_2\text{O})_x$ complexes ($x = 2 - 8$). *J. Phys. Chem. A* **2012**, 116, 3802–3815.

(172) Carl, D. R.; Chatterjee, B. K.; Armentrout, P. B. Threshold collision-induced dissociation of $\text{Sr}^{2+}(\text{H}_2\text{O})_x$ complexes ($x = 1 - 6$): An experimental and theoretical investigation of the complete inner shell hydration energies of Sr^{2+} . *J. Chem. Phys.* **2010**, 132, 044303.

(173) Wheeler, O. W.; Carl, D. R.; Hofstetter, T. E.; Armentrout, P. B. Hydration Enthalpies of $\text{Ba}^{2+}(\text{H}_2\text{O})_x$, $x = 1 - 8$: A Threshold Collision-Induced Dissociation and Computational Investigation. *J. Phys. Chem. A* **2015**, 119, 3800–3815.

(174) Hofstetter, T. E.; Armentrout, P. B. Threshold Collision-Induced Dissociation and Theoretical Studies of Hydrated $\text{Fe}(\text{II})$: Binding Energies and Coulombic Barrier Heights. *J. Phys. Chem. A* **2013**, 117, 1110–1123.

(175) Cooper, T. E.; Carl, D. R.; Armentrout, P. B. Hydration Energies of Zinc (II): Threshold Collision-induced Dissociation Experiments and Theoretical Studies. *J. Phys. Chem. A* **2009**, 113, 13727–13741.

(176) Cooper, T. E.; Armentrout, P. B. Threshold Collision-induced Dissociation of Hydrated Cadmium (II): Experimental and Theoretical Investigation of the Binding Energies for $\text{Cd}^{2+}(\text{H}_2\text{O})_n$ Complexes ($n = 4 - 11$). *Chem. Phys. Lett.* **2010**, 486, 1–6.

(177) Cooper, T. E.; Armentrout, P. B. Sequential bond energies and barrier heights for the water loss and charge separation dissociation pathways of $\text{Cd}^{2+}(\text{H}_2\text{O})_n$, $n = 3 - 11$. *J. Chem. Phys.* **2011**, 134, 114308.

(178) Sweeney, A. F.; Armentrout, P. B. Hydrated Copper Ion Chemistry: Guided Ion Beam and Computational Investigation of $\text{Cu}^{2+}(\text{H}_2\text{O})_n$ ($n = 7 - 10$) Complexes. *Eur. Mass Spectrom.* **2015**, 21, 497–516.

(179) Cooper, T. E.; O'Brien, J. T.; Williams, E. R.; Armentrout, P. B. Zn^{2+} has a Primary Hydration Sphere of Five: IR Action Spectroscopy and Theoretical Studies of Hydrated Zn^{2+} Complexes. *J. Phys. Chem. A* **2010**, 114, 12646–12655.

- (180) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. Hydration energies and structures of alkaline earth metal ions, $M^{2+}(H_2O)_n$, $n = 5-7$, $M = Mg, Ca, Sr$, and Ba . *J. Am. Chem. Soc.* **1999**, *121*, 8898–8906.
- (181) Wong, R. L.; Paech, K.; Williams, E. R. Blackbody infrared radiative dissociation at low temperature: hydration of $X^{2+}(H_2O)_n$ for $X = Mg, Ca$. *Int. J. Mass Spectrom.* **2004**, *232*, 59–66.
- (182) Peschke, M.; Blades, A. T.; Kebarle, P. Hydration energies and entropies for Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} from gas-phase ion-water molecule equilibria determinations. *J. Phys. Chem. A* **1998**, *102*, 9978–9985.
- (183) Blades, A. T.; Jayaweera, P.; Ikononou, M. G.; Kebarle, P. Studies of alkaline earth and transition metal M^{+2} gas phase ion chemistry. *J. Chem. Phys.* **1990**, *92*, 5900–5906.
- (184) Blades, A. T.; Jayaweera, P.; Ikononou, M. G.; Kebarle, P. Ion–molecule clusters involving doubly charged metal ions (M^{2+}). *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 251–267.
- (185) Davidson, W. R.; Kebarle, P. Ionic Solvation by Aprotic Solvents. Gas Phase Solvation of the Alkali Metal Ions by Acetonitrile. *J. Am. Chem. Soc.* **1976**, *98*, 6125–6133.
- (186) Bouchard, F.; Brenner, V.; Carra, C.; Hepburn, J. W.; Koyanagi, G. K.; McMahon, T. B.; Ohanessian, G.; Peschke, M. Energetics and structure of complexes of Al^+ with small organic molecules in the gas phase. *J. Phys. Chem. A* **1997**, *101*, 5885–5894.
- (187) Staley, R. H.; Beauchamp, J. L. Intrinsic acid-base properties of molecules. Binding energies of Li^+ to pi and n-donor bases. *J. Am. Chem. Soc.* **1975**, *97*, 5920–5921.
- (188) Uppal, J. S.; Staley, R. H. Relative binding energies of organic molecules to aluminum(+) ion in the gas phase. *J. Am. Chem. Soc.* **1982**, *104*, 1235–1238.
- (189) Gal, J.-F.; Taft, R. W.; McIver, R. T. Cationization by laser generation of aluminum ions: a basicity scale relative to Al^+ . *Spectrosc. Int. J.* **1984**, *3*, 96–104.
- (190) Valina, A. B.; Amunugama, R.; Huang, H.; Rodgers, M. T. Collision-Induced Dissociation and Theoretical Studies of Na^+ -Acetonitrile Complexes. *J. Phys. Chem. A* **2001**, *105*, 11057–11068.
- (191) Vitale, G.; Valina, A. B.; Huang, H.; Amunugama, R.; Rodgers, M. T. Solvation of Copper Ions by Acetonitrile. Structures and Sequential Binding Energies of $Cu^+(CH_3CN)_x$, $x = 1-5$ from Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2001**, *105*, 11351–11364.
- (192) Magnera, T. F.; David, D. E.; Michl, J. Gas-phase water and hydroxyl binding energies for mononuclear first-row transition metal ions. *J. Am. Chem. Soc.* **1989**, *111*, 4100–4101.
- (193) Kemper, P. R.; Bushnell, J. E.; Maitre, P.; Bowers, M. T. Comment on "The Origin of Anomalous Bond Dissociation Energies of $V^+(H_2)_n$ Clusters". *Chem. Phys. Lett.* **1995**, *242*, 244–248.
- (194) Perry, R. A.; Rowe, B. R.; Viggiano, A. A.; Albritton, D. L.; Ferguson, E. E.; Fehsenfeld, F. C. Laboratory measurements of stratospheric sodium ion reactions. *Geophys. Res. Lett.* **1980**, *7*, 693–696.
- (195) Dieterle, M.; Harvey, J. N.; Heinemann, C.; Schwarz, J.; Schröder, D.; Schwarz, H. Equilibrium studies of weakly bound $Fe(L)^+$ complexes with $L = Xe, CO_2, N_2$ and CH_4 . *Chem. Phys. Lett.* **1997**, *277*, 399–405.
- (196) Rodgers, M. T.; Armentrout, P. B. A Critical Evaluation of the Experimental and Theoretical Determination of Lithium Cation Affinities. *Int. J. Mass Spectrom.* **2007**, *267*, 167–182.
- (197) Peterson, K. I.; Mark, T. D.; Keesee, R. G.; Castleman, A. W. Thermochemical properties of gas-phase mixed clusters H_2O/CO_2 with Na^+ . *J. Phys. Chem.* **1984**, *88*, 2880–2883.
- (198) Yeh, C. S.; Willey, K. F.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. Photodissociation spectroscopy of the Mg^+-CO_2 complex and its isotopic analogs. *J. Chem. Phys.* **1993**, *98*, 1867–1875.
- (199) Armentrout, P. B.; Koizumi, H.; MacKenna, M. Sequential bond energies of $Fe^+(CO_2)_n$, $n = 1-5$, determined by threshold collision-induced dissociation and ab initio theory. *J. Phys. Chem. A* **2005**, *109*, 11365–11375.
- (200) Capron, L.; Feng, W. Y.; Lifshitz, C.; Tjelta, B. L.; Armentrout, P. B. Reactions and Thermochemistry of Small Cluster Ions: $Fe(CS_2)_n^+$ ($n = 1, 2$). *J. Phys. Chem.* **1996**, *100*, 16571–16576.
- (201) Haynes, C. L.; Fisher, E. R.; Armentrout, P. B. Probing The $[CoC_2H_6]^+$ Potential Energy Surface: A Detailed Guided-Ion Beam Study. *J. Am. Chem. Soc.* **1996**, *118*, 3269–3280.
- (202) Schultz, R. H.; Armentrout, P. B. Threshold Collisional Activation of $FeC_2H_6^+$: Fe^+ -ethane vs. Fe^+ -dimethyl Structures. *J. Phys. Chem.* **1992**, *96*, 1662–1667.
- (203) Zhang, Q.; Kemper, P. R.; Shin, S. K.; Bowers, M. T. Sigma bond activation by transition metal ions: the $Co(CH_4)_n^+$ systems revisited. *Int. J. Mass Spectrom.* **2001**, *204*, 281–294.
- (204) Kemper, P. R.; Bushnell, J.; van Koppen, P.; Bowers, M. T. Binding energies of $Co^+ \cdot (H_2/CH_4/C_2H_6)_{1,2,3}$ clusters. *J. Phys. Chem.* **1993**, *97*, 1810–1817.
- (205) van Koppen, P. A. M.; Perry, J. K.; Kemper, P. R.; Bushnell, J. E.; Bowers, M. T. Activation of Methane by Ti^+ : A Cluster Assisted Mechanism for σ -Bond Activation: Experiment and Theory. *Int. J. Mass Spectrom.* **1999**, *185–187*, 989–1001.
- (206) Zhang, Q.; Kemper, P. R.; Bowers, M. T. $Fe(CH_4)_n^+$ and $Ni(CH_4)_n^+$ clusters: Experimental and theoretical bond energies for $n = 1-6$. *Int. J. Mass Spectrom.* **2001**, *210–211*, 265–281.
- (207) Carpenter, C. J.; van Koppen, P. A. M.; Kemper, P. R.; Bushnell, J. E.; Weis, P.; Perry, J. K.; Bowers, M. T. Clustering and Activation in Reactions of $CoCp^+$ with Hydrogen and Methane. *Int. J. Mass Spectrom.* **2003**, *230*, 161–174.
- (208) Corderman, R. R.; Beauchamp, J. L. Quantitative Metal-Ligand Bond Dissociation Energies in the Gas Phase by Ion Cyclotron Resonance Spectroscopy. *J. Am. Chem. Soc.* **1976**, *98*, 3998–4000.
- (209) Klassen, J. S.; Anderson, S. G.; Blades, A. T.; Kebarle, P. Reaction enthalpies for $M^+L = M^+ + L$, where $M^+ = Na^+$ and K^+ and $L =$ acetamide, N-methylacetamide, N,N-dimethylacetamide, glycine, and glycylglycine, from determinations of the collision-induced dissociation thresholds. *J. Phys. Chem.* **1996**, *100*, 14218–14227.
- (210) Mayeux, C.; Tammiku-Taul, J.; Massi, L.; Gal, J.-F.; Burk, P. Interaction between the Cesium Cation and Cesium Carboxylates: An Extended Cs^+ Basicity Scale. *ChemPlusChem* **2013**, *78*, 1195–1204.
- (211) Chen, L.-Z.; Miller, J. M. Relative Metal Ion Affinities of Organic Nitriles in the Gas Phase. *Org. Mass Spectrom.* **1992**, *27*, 883–890.
- (212) More, M. B.; Glendening, E. D.; Ray, D.; Feller, D.; Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Bond Dissociation Energies and Equilibrium Structures of $Li^+[O(CH_3)_2]_x$, $x = 1-4$. *J. Phys. Chem.* **1996**, *100*, 1605–1614.
- (213) Huang, H.; Rodgers, M. T. Sigma versus Pi Interactions in Alkali Metal Ion Binding Affinities of Azoles: Threshold Collision-Induced Dissociation and Ab Initio Theory Studies. *J. Phys. Chem. A* **2002**, *106*, 4277–4289.
- (214) Rodgers, M. T.; Armentrout, P. B. Absolute Alkali Metal Ion Binding Affinities of Several Azoles Determined by Threshold Collision-Induced Dissociation. *Int. J. Mass Spectrom.* **1999**, *185–187*, 359–380.
- (215) Amunugama, R.; Rodgers, M. T. Absolute Alkali Metal Ion Binding Affinities of Several Azines Determined by Threshold Collision-Induced Dissociation and Ab Initio Theory. *Int. J. Mass Spectrom.* **2000**, *195–196*, 439–457.
- (216) Rodgers, M. T. Substituent Effects in the Binding of Alkali Metal Ions to Pyridines Studied by Threshold Collision-Induced Dissociation and Ab Initio Theory: The Aminopyridines. *J. Phys. Chem. A* **2001**, *105*, 8145–8153.
- (217) Rodgers, M. T.; Armentrout, P. B. Absolute Binding Energies of Sodium Ions to Short Chain Alcohols Determined by TCID Experiments and Ab Initio Theory. *J. Phys. Chem. A* **1999**, *103*, 4955–4963.
- (218) Amicangelo, J. C.; Armentrout, P. B. Relative and Absolute Bond Dissociation Energies of Sodium Cation–Alcohol Complexes Determined Using Competitive Collision-Induced Dissociation Experiments. *Int. J. Mass Spectrom.* **2011**, *301*, 45–54.

- (219) Moision, R. M.; Armentrout, P. B. An Experimental and Theoretical Dissection of Sodium Cation/Glycine Interactions. *J. Phys. Chem. A* **2002**, *106*, 10350–10362.
- (220) Rannulu, N. S.; Amunugama, R.; Yang, Z.; Rodgers, M. T. Influence of s and d Orbital Occupation on the Binding of Metal Ions to Imidazole. *J. Phys. Chem. A* **2004**, *108*, 6385–6396.
- (221) Guo, B. C.; Conklin, B. J.; Castleman, A. W. Thermochemical Properties of Ion Complexes $\text{Na}^+(\text{M})_n$ in the Gas Phase. *J. Am. Chem. Soc.* **1989**, *111*, 6506–6510.
- (222) Tsang, Y.; Siu, F. M.; Ho, C. S.; Ma, N. L.; Tsang, C. W. Experimental validation of theoretical potassium and sodium cation affinities of amides by mass spectrometric kinetic method measurements. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 345–355.
- (223) Sunner, J.; Kébarle, P. Ion-Solvent Molecule Interactions in the Gas-Phase. The Potassium Ion and Me_2SO , DMA, DMF and Acetone. *J. Am. Chem. Soc.* **1984**, *106*, 6135–6139.
- (224) Evans, D. H.; Keese, R. G.; Castleman, A. W. Thermodynamics of Gas-Phase Mixed-Solvent Cluster Ions: Water and Methanol on K^+ and Cl^- and Comparison to Liquid Solutions. *J. Phys. Chem.* **1991**, *95*, 3558–3564.
- (225) More, M. B.; Ray, D.; Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Bond Dissociation Energies of $\text{K}^+(\text{dimethyl ether})_x$, $x = 1 - 4$; $\text{K}^+(1,2\text{-dimethoxyethane})_x$, $x = 1$ and 2; and $\text{K}^+(12\text{-crown-4})$. *J. Phys. Chem. A* **1997**, *101*, 4254–4262.
- (226) Moision, R. M.; Armentrout, P. B. An Experimental and Theoretical Dissection of Potassium Cation/Glycine Interactions. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2588–2599.
- (227) Ruan, C.; Yang, Z.; Rodgers, M. T. Cation-p Interactions with a p-Excessive Nitrogen Heterocycle: Structures and Absolute Binding Energies of Alkali Metal Cation-Pyrrole complexes. *Int. J. Mass Spectrom.* **2007**, *267*, 233–247.
- (228) Opetri, L.; Tews, E. C.; Freiser, B. S. Determination of gas-phase ligand binding energies to Mg^+ by FTMS techniques. *J. Am. Chem. Soc.* **1988**, *110*, 3847–3853.
- (229) Rodgers, M. T.; Stanley, J. R.; Amunugama, R. Periodic Trends in the Binding of Metal Ions to Pyridine Studied by Threshold Collision-Induced Dissociation and Density Functional Theory. *J. Am. Chem. Soc.* **2000**, *122*, 10969–10978.
- (230) Amunugama, R.; Rodgers, M. T. Periodic Trends in the Binding of Metal Ions to Pyrimidine Studied by Threshold Collision-Induced Dissociation and Density Functional Theory. *J. Phys. Chem. A* **2001**, *105*, 9883–9892.
- (231) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gaussian-4 theory. *J. Chem. Phys.* **2007**, *126*, 084108.
- (232) Stoeckigt, D.; Holthausen, M. C.; Koch, W.; Schwarz, H. Theoretical Study of the $[\text{AlH}_2\text{C}_2\text{N}]^+$ Potential Energy Surface Combined with Experimental Investigations on $\text{Al}(\text{HCN})^+$. *J. Phys. Chem.* **1995**, *99*, S950–S955.
- (233) Meyer, F.; Khan, F. A.; Armentrout, P. B. Thermochemistry of Transition Metal Benzene Complexes: Binding Energies of $\text{M}(\text{C}_6\text{H}_6)_x^+$ ($x = 1, 2$) for $\text{M} = \text{Ti}$ to Cu . *J. Am. Chem. Soc.* **1995**, *117*, 9740–9748.
- (234) Koizumi, H.; Larsen, M.; Armentrout, P. B.; Feller, D. Collision-Induced Dissociation and Theoretical Studies of $\text{Ag}^+(\text{methanol})_n$, $n = 1 - 4$. *J. Phys. Chem. A* **2003**, *107*, 2329–2838.
- (235) Romanov, V.; Siu, C.-K.; Verkerk, U. H.; Aribi, H. E.; Hopkinson, A. C.; Siu, K. W. M. Binding Energies of the Silver Ion to Alcohols and Amides: A Theoretical and Experimental Study. *J. Phys. Chem. A* **2008**, *112*, 10912–10920.
- (236) Shoenib, T.; El Aribi, H.; Siu, K. W. M.; Hopkinson, A. C. A Study of Silver (I) Ion–Organonitrile Complexes: Ion Structures, Binding Energies, and Substituent Effects. *J. Phys. Chem. A* **2001**, *105*, 710–719.
- (237) Ho, Y.-P.; Yang, Y.-C.; Klippenstein, S. J.; Dunbar, R. C. Binding energies of Ag^+ and Cd^+ complexes from analysis of radiative association. *J. Phys. Chem. A* **1997**, *101*, 3338–3347.
- (238) Willey, K. F.; Cheng, P. Y.; Bishop, M. B.; Duncan, M. A. Charge-transfer photochemistry in ion–molecule cluster complexes of silver. *J. Am. Chem. Soc.* **1991**, *113*, 4721–4728.
- (239) Rodgers, M. T.; Armentrout, P. B. Influence of d Orbital Occupation on the Binding of Metal Ions to Adenine. *J. Am. Chem. Soc.* **2002**, *124*, 2678–2691.
- (240) Rannulu, N. S.; Rodgers, M. T. Noncovalent Interactions of Ni^+ with N-Donor Ligands (Pyridine, 4,4'-Dipyridyl, 2,2'-Dipyridyl, and 1,10-Phenanthroline): Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2009**, *113*, 4534–4548.
- (241) Ma, S.; Wong, P.; Yang, S. S.; Cooks, R. G. Gas-Phase Molecular, Molecular Pair, and Molecular Triplet Fe^+ Affinities of Pyridines. *J. Am. Chem. Soc.* **1996**, *118*, 6010–6019.
- (242) Wong, P. S. H.; Ma, S.; Wang, F.; Cooks, R. G. Stereoelectronic effects and gas phase Co^+ , Ni^+ , CpFe^+ , CpCo^+ and CpNi^+ affinities of pyridines studied by the kinetic method. *J. Organomet. Chem.* **1997**, *539*, 131–139.
- (243) Miller, K. J. Additivity Methods in Molecular Polarizability. *J. Am. Chem. Soc.* **1990**, *112*, 8533–8542.
- (244) Nielsen, S. B.; Masella, M.; Kébarle, P. Competitive Gas-Phase Solvation of Alkali Metal Ions by Water and Methanol. *J. Phys. Chem. A* **1999**, *103*, 9891–9898.
- (245) Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. Conversion of CH_4 to CH_3OH : Reactions of CoO^+ with CH_4 and D_2 , Co^+ with CH_3OD and D_2O , and $\text{Co}^+(\text{CH}_3\text{OD})$ with Xe . *J. Am. Chem. Soc.* **1994**, *116*, 7815–7826.
- (246) Yang, Z.; Rannulu, N. S.; Chu, Y.; Rodgers, M. T. Bond Dissociation Energies and Equilibrium Structures of $\text{Cu}^+(\text{MeOH})_x$, $x = 1-6$, in the Gas Phase: Competition between Solvation of the Metal Ion and Hydrogen-Bonding Interactions. *J. Phys. Chem. A* **2008**, *112*, 388–401.
- (247) Chu, Y.; Yang, Z.; Rodgers, M. T. Solvation of Copper Ions by Acetone. Structures and Sequential Binding Energies of $\text{Cu}^+(\text{acetone})_x$, $x = 1-4$ from Collision-Induced Dissociation and Theoretical Studies. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 453–468.
- (248) Rannulu, N. S.; Rodgers, M. T. Solvation of Copper Ions by Imidazole: Structures and Sequential Binding Energies of $\text{Cu}^+(\text{imidazole})_x$, $x = 1-4$. Competition between Ion Solvation and Hydrogen Bonding. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1014–1025.
- (249) Davidson, W. R.; Kébarle, P. Binding energies and stabilities of potassium ion complexes with ethylene diamine and dimethoxyethane (glyme) from measurements of the complexing equilibria in the gas phase. *Can. J. Chem.* **1976**, *54*, 2594–2599.
- (250) Yang, Y.-S.; Hsu, W.-Y.; Lee, H.-F.; Huang, Y.-C.; Yeh, C.-S.; Hu, C.-H. Experimental and Theoretical Studies of Metal Cation–Pyridine Complexes Containing Cu and Ag. *J. Phys. Chem. A* **1999**, *103*, 11287–11292.
- (251) Nose, H.; Chen, Y.; Rodgers, M. T. Energy-Resolved Collision-Induced Dissociation Studies of 1,10-Phenanthroline Complexes of the Late First-Row Divalent Transition Metal Cations: Determination of the Third Sequential Binding Energies. *J. Phys. Chem. A* **2013**, *117*, 4316–4330.
- (252) Jones, R. W.; Staley, R. H. Relative bond dissociation energies for two-ligand complexes of cobalt(1+) with organic molecules in the gas phase. *J. Phys. Chem.* **1982**, *86*, 1387–1392.
- (253) Jones, R. W.; Staley, R. H. Relative Bond Dissociation Energies for Two-Ligand Complexes of Cu^+ with Organic Molecules in the Gas Phase. *J. Am. Chem. Soc.* **1982**, *104*, 2296–2300.
- (254) Deng, H.; Kébarle, P. Bond Energies of Copper Ion-Ligand L Complexes CuL_2^+ Determined in the Gas Phase by Ion-Ligand Exchange Equilibria Measurements. *J. Am. Chem. Soc.* **1998**, *120*, 2925–2931.
- (255) Deng, H.; Kébarle, P. Binding Energies of Silver Ion-Ligand, L, Complexes AgL_2^+ Determined from Ligand-Exchange Equilibria in the Gas Phase. *J. Phys. Chem. A* **1998**, *102*, 571–579.
- (256) Langhoff, S. R.; Bauschlicher, C. W., Jr.; Partridge, H.; Sodupe, M. Theoretical Study of One and Two Ammonia Molecules bound to the First-Row Transition Metal Ions. *J. Phys. Chem.* **1991**, *95*, 10677–10681.
- (257) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. The Binding Energies of $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Cu}^+(\text{NH}_3)_n$ ($n = 1-4$). *J. Chem. Phys.* **1991**, *94*, 2068–2072.

- (258) Schalley, C. A. Supramolecular Chemistry Goes Gas Phase: The Mass Spectrometric Examination of Noncovalent Interactions in Host–guest Chemistry and Molecular Recognition. *Int. J. Mass Spectrom.* **2000**, *194*, 11–39.
- (259) Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Thermodynamic Insight into Molecular Recognition. *Int. J. Mass Spectrom.* **1999**, *193*, 227–240.
- (260) More, M. B.; Ray, D.; Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Bond Dissociation Energies of $\text{Na}^+(\text{dimethyl ether})_x$, $x = 1 - 4$; $\text{Na}^+(1,2\text{-dimethoxyethane})_x$, $x = 1$ and 2 ; and $\text{Na}^+(12\text{-crown-4})$. *J. Phys. Chem. A* **1997**, *101*, 831–839.
- (261) More, M. B.; Ray, D.; Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Bond Dissociation Energies of $\text{M}^+(\text{dimethyl ether})_x$, $x = 1 - 3$, $\text{M}^+(1,2\text{-dimethoxyethane})_x$, $x = 1$ and 2 , and $\text{M}^+(12\text{-crown-4})$ Where $\text{M} = \text{Rb}$ and Cs . *J. Phys. Chem. A* **1997**, *101*, 7007–7017.
- (262) Ray, D.; Feller, D.; More, M. B.; Glendening, E. D.; Armentrout, P. B. Cation-Ether Complexes in the Gas Phase: Bond Dissociation Energies and Equilibrium Structures of $\text{Li}^+[1,2\text{-dimethoxyethane}]_x$, $x = 1-2$, and $\text{Li}^+[12\text{-crown-4}]$. *J. Phys. Chem.* **1996**, *100*, 16116–16125.
- (263) Armentrout, P. B.; Austin, C. A.; Rodgers, M. T. Alkali Metal Cation Interactions with 12-Crown-4 in the Gas Phase: Revisited. *Int. J. Mass Spectrom.* **2012**, *330–332*, 16–26.
- (264) Austin, C. A.; Chen, Y.; Rodgers, M. T. Alkali Metal Cation-Cyclen Complexes: Effects of Alkali Metal Cation Size on the Structure and Binding Energy. *Int. J. Mass Spectrom.* **2012**, *330–332*, 27–34.
- (265) More, M. B.; Ray, D.; Armentrout, P. B. Intrinsic Affinities of Alkali Cations for 15-Crown-5 and 18-Crown-6: Bond Dissociation Energies of Gas-Phase M^+ -Crown Ether Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 417–423.
- (266) Armentrout, P. B.; Austin, C. A.; Rodgers, M. T. Alkali Metal Cation Interactions with 15-Crown-5 in the Gas Phase: Revisited. *J. Phys. Chem. A* **2014**, *118*, 8088–8097.
- (267) Austin, C. A.; Rodgers, M. T. Intrinsic Affinities of Alkali Metal Cations for Diaza-18-crown-6: Effects of Alkali Metal Cation Size and Donor Atoms on the Binding Energies. *Int. J. Mass Spectrom.* **2015**, *377*, 64–72.
- (268) Austin, C. A.; Rodgers, M. T. Alkali metal Cation-Hexacyclen Complexes: Effects of Alkali metal Cation Size on the Structure and Binding Energy. *J. Phys. Chem. A* **2014**, *118*, 5488–5500.
- (269) Nicoll, J. B.; Dearden, D. V. Reactions of multidentate ligands with ligated alkali cation complexes: self-exchange and “sandwich” complex formation kinetics of gas phase crown ether–alkali cation complexes. *Int. J. Mass Spectrom.* **2001**, *204*, 171–183.
- (270) Anderson, J. D.; Paulsen, E. S.; Dearden, D. V. Alkali metal binding energies of dibenzo-18-crown-6: Experimental and computational results. *Int. J. Mass Spectrom.* **2003**, *227*, 63–76.
- (271) Chinthaka, S. D. M.; Chu, Y.; Rannulu, N. S.; Rodgers, M. T. Sodium Cation Affinities of MALDI Matrices Determined by Guided Ion Beam Tandem Mass Spectrometry: Application to Benzoic acid Derivatives. *J. Phys. Chem. A* **2006**, *110*, 1426–1437.
- (272) Chinthaka, S. D. M.; Rodgers, M. T. Sodium Cation Affinities of Commonly Used MALDI Matrices Determined by Guided Ion Beam Tandem Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* **2012**, *23*, 676–689.
- (273) Chinthaka, S. D. M.; Rodgers, M. T. Potassium Cation Affinities of Matrix Assisted Laser Desorption Ionization Matrices Determined by Threshold Collision-Induced Dissociation: Application to Benzoic acid Derivatives. *J. Phys. Chem. A* **2007**, *111*, 8152–8162.
- (274) Zhang, J.; Knochenmuss, R.; Stevenson, E.; Zenobi, R. The Gas-Phase Sodium Basicities of Common Matrix-Assisted Laser Desorption/Ionization Matrices. *Int. J. Mass Spectrom.* **2002**, *213*, 237–250.
- (275) Zhang, J.; Dyachokva, E.; Ha, T.-K.; Knochenmuss, R.; Zenobi, R. Gas-Phase Potassium Binding Energies of MALDI Matrices: An Experimental and Theoretical Study. *J. Phys. Chem. A* **2003**, *107*, 6891–6900.
- (276) Guo, B. C.; Castleman, A. W., Jr. The bonding strength of $\text{Ag}^+(\text{C}_2\text{H}_4)$ and $\text{Ag}^+(\text{C}_2\text{H}_4)_2$ complexes. *Chem. Phys. Lett.* **1991**, *181*, 16–20.
- (277) Sunner, J.; Nishizawa, K.; Kebarle, P. Ion-Solvent Molecule Interactions in the Gas Phase. The Potassium Ion and Benzene. *J. Phys. Chem.* **1981**, *85*, 1814–1820.
- (278) Amicangelo, J. C.; Armentrout, P. B. Absolute Binding Energies of Alkali-Metal Cation Complexes with Benzene Determined by Threshold Collision-Induced Dissociation Experiments and Ab Initio Theory. *J. Phys. Chem. A* **2000**, *104*, 11420–11432.
- (279) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr. The Clustering Reactions of Benzene with Sodium and Lead. *Chem. Phys. Lett.* **1990**, *168*, 155.
- (280) Willey, K. F.; Yeh, C. S.; Robbins, D. L.; Duncan, M. A. Charge-transfer in the photodissociation of metal ion-benzene complexes. *J. Phys. Chem.* **1992**, *96*, 9106–9111.
- (281) Bauschlicher, C. W., Jr.; Partridge, H. Mg^+ -ligand binding energies. *Chem. Phys. Lett.* **1991**, *181*, 129–133.
- (282) Dunbar, R. C.; Klippenstein, S. J.; Hrusak, J.; Stockigt, D.; Schwarz, H. Binding Energy of $\text{Al}(\text{C}_6\text{H}_6)^+$ from Analysis of Radiative Association Kinetics. *J. Am. Chem. Soc.* **1996**, *118*, 5277–5283.
- (283) Hettich, R. L.; Freiser, B. S. Spectroscopic and Thermodynamic Investigations of Transition-metal Cluster Ions in the Gas Phase: Photodissociation of MFe^+ . *J. Am. Chem. Soc.* **1987**, *109*, 3537–3542.
- (284) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. Gas-Phase Photodissociation of Organometallic Ions: Bond Energy and Structure Determinations. *J. Am. Chem. Soc.* **1986**, *108*, 5086–5093.
- (285) Afzaal, S.; Freiser, B. S. Gas-phase photodissociation study of $\text{Ag}(\text{benzene})^+$ and $\text{Ag}(\text{toluene})^+$. *Chem. Phys. Lett.* **1994**, *218*, 254–260.
- (286) Freiser, B. S. Methods for Determining Metal-Ligand and Metal-Metal Bond Energies Using Fourier Transform Mass Spectrometry. *ACS Symp. Series* **1990**, *428*, 55–69.
- (287) Lin, C.-Y.; Dunbar, R. C. Radiative Association Kinetics and Binding Energies of Chromium Ions with Benzene and Benzene Derivatives. *Organometallics* **1997**, *16*, 2691–2697.
- (288) Lin, C.-Y.; Chen, Q.; Chen, H.; Freiser, B. S. Observing Unimolecular Dissociation of Metastable Ions in FT-ICR: A Novel Application of the Continuous Ejection Technique. *J. Phys. Chem. A* **1997**, *101*, 6023–6029.
- (289) Chen, Y. M.; Armentrout, P. B. Collision Induced Dissociation of $\text{Ag}(\text{C}_6\text{H}_6)^+$. *Chem. Phys. Lett.* **1993**, *210*, 123–128.
- (290) Ruan, C.; Yang, Z.; Rodgers, M. T. Influence of the d Orbital Occupation on the Nature and Strength of Copper Cation-p Interactions: Threshold Collision-Induced Dissociation and Theoretical Studies. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5902–5918.
- (291) Gapeev, A.; Yang, C.-N.; Klippenstein, S. J.; Dunbar, R. C. Binding Energies of Gas-Phase Metal Ions with Pyrrole: Experimental and Quantum Chemical Results. *J. Phys. Chem. A* **2000**, *104*, 3246–3256.
- (292) Amunugama, R.; Rodgers, M. T. The Influence of Substituents on Cation-p Interactions. 1. Absolute Binding Energies of Alkali Metal Cation-Toluene Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2002**, *106*, 5529–5539.
- (293) Gal, J.-F.; Maria, P.-C.; Decouzon, M.; M6, O.; Y6ñez, M. Gas-phase Lithium-Cation Basicities of Some Benzene Derivatives. An Experimental and Theoretical Study. *Int. J. Mass Spectrom.* **2002**, *219*, 445–456.
- (294) Amunugama, R.; Rodgers, M. T. The Influence of Substituents on Cation-p Interactions. 3. Absolute Binding Energies of Alkali Metal Cation-Aniline Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *Int. J. Mass Spectrom.* **2003**, *227*, 339–360.
- (295) Hallowita, N.; Carl, D. R.; Armentrout, P. B.; Rodgers, M. T. Dipole Effects on Cation- π Interactions: Absolute Bond Dissociation Energies of Complexes of Alkali Metal Cations to N-methylaniline and N,N-dimethylaniline. *J. Phys. Chem. A* **2008**, *112*, 7996–8008.

- (296) Amunugama, R.; Rodgers, M. T. The Influence of Substituents on Cation- π Interactions. 4. Absolute Binding Energies of Alkali Metal Cation-Phenol Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2002**, *106*, 9718–9728.
- (297) Ryzhov, V.; Dunbar, R. C. Interactions of phenol and indole with metal ions in the gas phase: Models for Tyr and Trp side-chain binding. *J. Am. Chem. Soc.* **1999**, *121*, 2259–2268.
- (298) Amunugama, R.; Rodgers, M. T. The Influence of Substituents on Cation- π Interactions. 5. Absolute Binding Energies of Alkali Metal Cation-Anisole Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *Int. J. Mass Spectrom.* **2003**, *222*, 431–450.
- (299) Hallowita, N.; Udonkang, E.; Ruan, C.; Frieler, C. E.; Rodgers, M. T. Inductive Effects of Cation- π Interactions: Structures and Bond Dissociation Energies of Alkali Metal Cation-Halobenzene Complexes. *Int. J. Mass Spectrom.* **2009**, *283*, 35–47.
- (300) Amunugama, R.; Rodgers, M. T. The Influence of Substituents on Cation- π Interactions. 2. Absolute Binding Energies of Alkali Metal Cation-Fluorobenzene Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2002**, *106*, 9092–9103.
- (301) Ruan, C.; Yang, Z.; Hallowita, N.; Rodgers, M. T. Cation- π Interactions with a Model for the Side Chain of Tryptophan: Structures and Absolute Binding Energies of Alkali Metal Cation-Indole Complexes. *J. Phys. Chem. A* **2005**, *109*, 11539–11550.
- (302) Amunugama, R.; Rodgers, M. T. Cation- π Interactions with a Model for an Extended π Network Absolute Binding Energies of Alkali Metal Cation-Naphthalene Complexes Determined by Threshold Collision-Induced Dissociation and Theoretical Studies. *Int. J. Mass Spectrom.* **2003**, *227*, 1–20.
- (303) Gal, J.-F.; Maria, P.-C.; Decouzon, M.; M $\acute{o}$, O.; Y $\acute{a}$ ñez, M.; Abboud, J. L. M. Lithium-Cation/ π Complexes of Aromatic Systems. The Effect of Increasing the Number of Fused Rings. *J. Am. Chem. Soc.* **2003**, *125*, 10394–10401.
- (304) Nanayakkara, V. K.; Freiser, B. S. Thermochemistry and Photodissociation Studies of $[\text{CoL}]^+$ and $[\text{CoL}_2]^+$, L = Pyrrole, Furan, Thiophene and Selenophene. *J. Mass Spectrom.* **1997**, *32*, 475–482.
- (305) Bakhtiar, R.; Jacobson, D. B. Transition-metal mediated heteroatom removal by reactions of FeL^+ [L = O, C_4H_6 , $\text{c-C}_5\text{H}_6$, $\text{c-C}_5\text{H}_5$, C_6H_6 , $\text{C}_5\text{H}_4(=\text{CH}_2)$] with furan, thiophene, and pyrrole in the gas phase. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 938–952.
- (306) Sunderlin, L.; Aristov, N.; Armentrout, P. B. Reaction of Scandium Ions with Ethane. First and Second Hydride Scandium Ion Bond Energies. *J. Am. Chem. Soc.* **1987**, *109*, 78–89.
- (307) Sunderlin, L. S.; Armentrout, P. B. Thermochemistry of Ti^+ -Hydrocarbon Bonds: Translational Energy Dependence of the Reactions of Ti^+ with Ethane, Propane, and Trans-2-Butene. *Int. J. Mass Spectrom. Ion Processes* **1989**, *94*, 149–177.
- (308) Aristov, N.; Armentrout, P. B. Reaction Mechanisms and Thermochemistry of $\text{V}^+ + \text{C}_2\text{H}_{2p}$ ($p = 1, 2, 3$). *J. Am. Chem. Soc.* **1986**, *108*, 1806–1819.
- (309) Georgiadis, R.; Armentrout, P. B. Reactions of Ground State Cr^+ with C_2H_6 , C_2H_4 , cyclo C_3H_6 , and cyclo $\text{C}_2\text{H}_4\text{O}$: Bond Energies for CrCH_n^+ ($n = 1-3$). *Int. J. Mass Spectrom. Ion Processes* **1989**, *89*, 227–247.
- (310) Sunderlin, L. S.; Armentrout, P. B. Thermochemistry of C H and C C Bond Activation: Translational Energy Dependence of Reactions of Sc^+ with Propane and 2-Butenes. *Organometallics* **1990**, *9*, 1248–1253.
- (311) Fisher, E. R.; Armentrout, P. B. Activation of Alkanes by Cr^+ : Unique Reactivity of Ground State $\text{Cr}^+(^6\text{S})$ and Thermochemistry of Neutral and Ionic Chromium-Carbon Bonds. *J. Am. Chem. Soc.* **1992**, *114*, 2039–2049.
- (312) Sunderlin, L. S.; Armentrout, P. B. Periodic Trends in Chemical Reactivity: Reactions of Sc^+ , Y^+ , La^+ , and Lu^+ with Methane and Ethane. *J. Am. Chem. Soc.* **1989**, *111*, 3845–3855.
- (313) Schultz, R. H.; Armentrout, P. B. Thermochemistry and Structures of FeC_3H_6^+ : Metallacycle and Metal-Alkene Isomers. *Organometallics* **1992**, *11*, 828–836.
- (314) Haynes, C. L.; Armentrout, P. B. Thermochemistry and Structures of CoC_3H_6^+ : Metallacycle and Metal-Alkene Isomers. *Organometallics* **1994**, *13*, 3480–3490.
- (315) Ruan, C.; Huang, H.; Rodgers, M. T. A Simple Model for Metal Cation-Phosphate Interactions in Nucleic Acids in the Gas Phase: Alkali Metal Cations and Trimethyl Phosphate. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 305–314.
- (316) Ruan, C.; Huang, H.; Rodgers, M. T. Modeling Metal Cation-Phosphate Interactions in Nucleic Acids in the Gas Phase: Alkali Metal Cations and Triethyl Phosphate. *J. Phys. Chem. A* **2007**, *111*, 13521–13527.
- (317) Armentrout, P. B.; Armentrout, E. I.; Clark, A. A.; Cooper, T. E.; Stennett, E. M. S.; Carl, D. R. An Experimental and Theoretical Study of Alkali Metal Cation Interactions with Cysteine. *J. Phys. Chem. B* **2010**, *114*, 3927–3937.
- (318) Mookherjee, A.; Armentrout, P. B. Theoretical Investigation and Reinterpretation of the Decomposition of Lithiated Proline and N-Methyl Proline. *Int. J. Mass Spectrom.* **2014**, *370*, 16–28.
- (319) Ye, S. J.; Clark, A. A.; Armentrout, P. B. An Experimental and Theoretical Investigation of Alkali Metal Cation Interactions with Hydroxyl Side Chain Amino Acids. *J. Phys. Chem. B* **2008**, *112*, 10291–10302.
- (320) Armentrout, P. B.; Gabriel, A.; Moision, R. M. An Experimental and Theoretical Study of Alkali Metal Cation/Methionine Interactions. *Int. J. Mass Spectrom.* **2009**, *283*, 56–68.
- (321) Moision, R. M.; Armentrout, P. B. The Special Five-membered Ring of Proline: An Experimental and Theoretical Investigation of Alkali Metal Cation Interactions with Proline and Its Four- and Six-membered Ring Analogues. *J. Phys. Chem. A* **2006**, *110*, 3933–3946.
- (322) Bojesen, G.; Breindahl, T.; Andersen, U. N. On the Sodium and Lithium Ion Affinities of Some α -Amino Acids. *Org. Mass Spectrom.* **1993**, *28*, 1448–1452.
- (323) Feng, W. Y.; Gronert, S.; Lebrilla, C. B. The Lithium Cation Binding Energies of Gaseous Amino Acids. *J. Phys. Chem. A* **2003**, *107*, 405–410.
- (324) Bourcier, S.; Chia, R. X.; Bimbong, R. N. B.; Bouchoux, G. Gas-phase lithium cation affinity of glycine. *Eur. J. Mass Spectrom.* **2015**, *21*, 149–159.
- (325) Mookherjee, A.; Armentrout, P. B. Role of Methylation on the Thermochemistry of Alkali Metal Cation Complexes of Amino Acids: N-Methyl Proline. *Int. J. Mass Spectrom.* **2013**, *345–347*, 109–119.
- (326) Heaton, A. L.; Moision, R. M.; Armentrout, P. B. Experimental and Theoretical Studies of Sodium Cation Interactions with the Acidic Amino Acids and Their Amide Derivatives. *J. Phys. Chem. A* **2008**, *112*, 3319–3327.
- (327) Ruan, C.; Rodgers, M. T. Cation- π Interactions: Structures and Energetics of Complexation of Na^+ and K^+ with the Aromatic Amino Acids, Phenylalanine, Tyrosine and Tryptophan. *J. Am. Chem. Soc.* **2004**, *126*, 14600–14610.
- (328) Armentrout, P. B.; Citir, M.; Chen, Y.; Rodgers, M. T. Thermochemistry of Alkali Metal Cation Interactions with Histidine: Influence of the Side-Chain. *J. Phys. Chem. A* **2012**, *116*, 11823–11832.
- (329) Gapeev, A.; Dunbar, R. C. Na^+ affinities of gas-phase amino acids by ligand exchange equilibrium. *Int. J. Mass Spectrom.* **2003**, *228*, 825–839.
- (330) Kish, M. M.; Ohanessian, G.; Wesdemiotis, C. The Na^+ affinities of α -amino acids: side-chain substituent effects. *Int. J. Mass Spectrom.* **2003**, *227*, 509–524.
- (331) Wang, P.; Ohanessian, G.; Wesdemiotis, C. The Sodium Ion Affinities of Asparagine, Glutamine, Histidine and Arginine. *Int. J. Mass Spectrom.* **2008**, *269*, 34–45.
- (332) Wang, P.; Wesdemiotis, C.; Kapota, C.; Ohanessian, G. The Sodium Ion Affinities of Simple Di-, Tri-, and Tetrapeptide. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 541–552.

- (333) Heaton, A. L.; Armentrout, P. B. Experimental and Theoretical Studies of Potassium Cation Interactions with the Acidic Amino Acids and Their Amide Derivatives. *J. Phys. Chem. B* **2008**, *112*, 12056–12065.
- (334) Tsang, Y.; Wong, C. C. L.; Wong, C. H. S.; Cheng, J. M. K.; Ma, N. L.; Tsang, C. W. Proton and potassium affinities of aliphatic and N-methylated aliphatic α -amino acids: Effect of alkyl chain length on relative stabilities of K^+ bound zwitterionic complexes. *Int. J. Mass Spectrom.* **2012**, *316*–318, 273–283.
- (335) Schäfer, M.; Drayss, M. K.; Blunk, D.; Purcell, J. M.; Hendrickson, C. L.; Marshall, A. G.; Mookherjee, A.; Armentrout, P. B. Kinetic Determination of Potassium Affinities by IRMPD: Elucidation of Precursor Ion Structures. *J. Phys. Chem. A* **2009**, *113*, 7779–7783.
- (336) Bowman, V. N.; Heaton, A. L.; Armentrout, P. B. Metal Cation Dependence of Interactions with Amino Acids: Bond Energies of Rb^+ to Gly, Ser, Thr, and Pro. *J. Phys. Chem. B* **2010**, *114*, 4107–4114.
- (337) Armentrout, P. B.; Chen, Y.; Rodgers, M. T. Metal Cation Dependence of Interactions with Amino Acids: Bond Energies of Cs^+ to Gly, Pro, Ser, Thr, and Cys. *J. Phys. Chem. A* **2012**, *116*, 3989–3999.
- (338) Armentrout, P. B.; Yang, B.; Rodgers, M. T. Metal Cation Dependence of Interactions with Amino Acids: Bond Dissociation Energies of Rb^+ and Cs^+ to the Acidic Amino Acids and Their Amide Derivatives. *J. Phys. Chem. B* **2014**, *118*, 4300–4314.
- (339) Armentrout, P. B.; Yang, B.; Rodgers, M. T. Metal Cation Dependence of Interactions with Amino Acids: Bond Energies of Rb^+ and Cs^+ to Met, Phe, Tyr, and Trp. *J. Phys. Chem. B* **2013**, *117*, 3771–3781.
- (340) Cerda, B. A.; Wesdemiotis, C. The Relative Copper(I) Ion Affinities of Amino Acids in the Gas Phase. *J. Am. Chem. Soc.* **1995**, *117*, 9734–9739.
- (341) Lee, V. W.-M.; Li, H.; Lau, T.-C.; Guevremont, R.; Siu, K. W. M. Relative silver(I) ion binding energies of α -amino acids: A determination by means of the kinetic method. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 760–766.
- (342) McMeekin, T. L.; Wilensky, M.; Groves, M. L. Refractive indices of proteins in relation to amino acid composition and specific volume. *Biochem. Biophys. Res. Commun.* **1962**, *7*, 151–156.
- (343) Kapota, C.; Lemaire, J.; Maitre, P.; Ohanessian, G. Vibrational Signature of Charge Solvation vs Salt Bridge Isomers of Sodiated Amino Acids in the Gas Phase. *J. Am. Chem. Soc.* **2004**, *126*, 1836–1842.
- (344) Drayss, M. K.; Blunk, D.; Oomens, J.; Schäfer, M. Infrared Multiple Photon Dissociation Spectroscopy of Potassiated Proline. *J. Phys. Chem. A* **2008**, *112*, 11972–11974.
- (345) Bush, M. F.; Oomens, J.; Saykally, R. J.; Williams, E. R. Effects of Alkaline Earth Metal Ion Complexation on Amino Acid Zwitterion Stability: Results from Infrared Action Spectroscopy. *J. Am. Chem. Soc.* **2008**, *130*, 6463–6471.
- (346) Bush, M. F.; Oomens, J.; Saykally, R. J.; Williams, E. R. Alkali Metal Ion Binding to Glutamine and Glutamine Derivatives Investigated by Infrared Action Spectroscopy and Theory. *J. Phys. Chem. A* **2008**, *112*, 8578–8584.
- (347) Polfer, N. C.; Oomens, J.; Dunbar, R. C. IRMPD Spectroscopy of Metal-Ion/Tryptophan Complexes. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2744–2751.
- (348) Dunbar, R. C.; Polfer, N. C.; Oomens, J. Gas-phase zwitterions stabilization by a metal dication. *J. Am. Chem. Soc.* **2007**, *129*, 14562–14563.
- (349) Bush, M. F.; Forbes, M. W.; Jockusch, R. A.; Oomens, J.; Polfer, N. C.; Saykally, R. J.; Williams, E. R. Infrared Spectroscopy of Cationized Lysine and ϵ -N-methyllysine in the Gas Phase: Effects of Alkali-Metal Ion Size and Proton Affinity on Zwitterion Stability. *J. Phys. Chem. A* **2007**, *111*, 7753–7760.
- (350) Bush, M. F.; Oomens, J.; Williams, E. R. Proton Affinity and Zwitterion Stability: New Results from Infrared Spectroscopy and Theory of Cationized Lysine and Analogues in the Gas Phase. *J. Phys. Chem. A* **2009**, *113*, 431–438.
- (351) Forbes, M. W.; Bush, M. F.; Polfer, N. C.; Oomens, J.; Dunbar, R. C.; Williams, E. R.; Jockusch, R. A. Infrared Spectroscopy of Arginine Cation Complexes: Direct Observation of Gas-Phase Zwitterions. *J. Phys. Chem. A* **2007**, *111*, 11759–11770.
- (352) Bush, M. F.; O'Brien, J. T.; Prell, J. S.; Saykally, R. J.; Williams, E. R. Infrared Spectroscopy of Cationized Arginine in the Gas Phase: Direct Evidence for the Transition from Nonzwitterionic to Zwitterionic Structure. *J. Am. Chem. Soc.* **2007**, *129*, 1612–1622.
- (353) Armentrout, P. B.; Rodgers, M. T.; Oomens, J.; Steill, J. D. Infrared Multiphoton Dissociation Spectroscopy of Cationized Serine: Effects of Alkali-Metal Cation Size on Gas-Phase Conformation. *J. Phys. Chem. A* **2008**, *112*, 2248–2257.
- (354) Rodgers, M. T.; Armentrout, P. B.; Oomens, J.; Steill, J. D. Infrared Multiphoton Dissociation Spectroscopy of Cationized Threonine: Effects of Alkali-Metal Cation Size on Gas-Phase Conformation. *J. Phys. Chem. A* **2008**, *112*, 2258–2267.
- (355) O'Brien, J. T.; Prell, J. S.; Steill, J. D.; Oomens, J.; Williams, E. R. Interactions of Mono- and Divalent Metal Ions with Aspartic and Glutamic Acid Investigated with IR Photodissociation Spectroscopy and Theory. *J. Phys. Chem. A* **2008**, *112*, 10823–10830.
- (356) Heaton, A. L.; Bowman, V. N.; Oomens, J.; Steill, J. D.; Armentrout, P. B. Infrared Multiple Photon Dissociation Spectroscopy of Cationized Asparagine: Effects of Alkali-Metal Cation Size on Gas-Phase Conformation. *J. Phys. Chem. A* **2009**, *113*, 5519–5530.
- (357) Carl, D. R.; Cooper, T. E.; Oomens, J.; Steill, J. D.; Armentrout, P. B. Infrared Multiple Photon Dissociation Spectroscopy of Cationized Methionine: Effects of Alkali-Metal Cation Size on Gas-Phase Conformation. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3384–3398.
- (358) Citir, M.; Stennett, E. M. S.; Oomens, J.; Steill, J. D.; Rodgers, M. T.; Armentrout, P. B. Infrared Multiple Photon Dissociation Spectroscopy of Cationized Cysteine: Effects of Metal Cation Size on Gas-Phase Conformation. *Int. J. Mass Spectrom.* **2010**, *297*, 9–17.
- (359) Rodgers, M. T.; Armentrout, P. B. In *The Alkali Metal Ions: Their Role for Life*; Sigel, A., Sigel, H., Sigel, R. K. O., Eds.; Metal Ions in Life Sciences 16; Springer: Cham, Switzerland, 2016; pp. 103–131.
- (360) Dunbar, R. C. In *Gas-Phase IR Spectroscopy and Structure of Biological Molecules*; Rijs, A. M., Oomens, J., Eds.; Springer: 2015.
- (361) Talley, J. M.; Cerda, B. A.; Ohanessian, G.; Wesdemiotis, C. Alkali Metal Ion Binding to Amino Acids Versus Their Methyl Esters: Affinity Trends and Structural Changes in the Gas Phase. *Chem. - Eur. J.* **2002**, *8*, 1377–1388.
- (362) Heaton, A. L.; Ye, S. J.; Armentrout, P. B. Experimental and Theoretical Studies of Sodium Cation Complexes of the Deamidation and Dehydration Products of Asparagine, Glutamine, Aspartic Acid, and Glutamic Acid. *J. Phys. Chem. A* **2008**, *112*, 3328–3338.
- (363) Ye, S. J.; Armentrout, P. B. An Experimental and Theoretical Investigation of the Decomposition of Lithiated Hydroxyl Side Chain Amino Acids. *J. Phys. Chem. B* **2008**, *112*, 10303–10313.
- (364) Armentrout, P. B.; Ye, S. J.; Gabriel, A.; Moision, R. M. Energetics and Mechanism for the Deamidation of Lithiated Cysteine. *J. Phys. Chem. B* **2010**, *114*, 3938–3949.
- (365) Ye, S. J.; Armentrout, P. B. Absolute Thermodynamic Measurements of Alkali Metal Cation Interactions with a Simple Dipeptide and Tripeptide. *J. Phys. Chem. A* **2008**, *112*, 3587–3596.
- (366) Cerda, B. A.; Hoyau, S.; Ohanessian, G.; Wesdemiotis, C. Na^+ binding to cyclic and linear dipeptides. Binding energies entropies of Na^+ complexation and attachment sites from the dissociation of Na^+ -bound heterodimers and ab initio calculations. *J. Am. Chem. Soc.* **1998**, *120*, 2437–2448.
- (367) Feng, W. Y.; Gronert, S.; Lebrilla, C. B. Lithium and Sodium Ion Binding Energies on N-Acetyl and N-Glycyl Amino Acids. *J. Am. Chem. Soc.* **1999**, *121*, 1365–1371.
- (368) Heaton, A. L.; Armentrout, P. B. Experimental and Theoretical Studies of Sodium Cation Interactions with D-Arabinose, Xylose, Glucose and Galactose. *J. Phys. Chem. A* **2008**, *112*, 10156–10167.
- (369) Cerda, B. A.; Wesdemiotis, C. Thermochemistry and structures of Na^+ coordinated mono- and disaccharide stereoisomers. *Int. J. Mass Spectrom.* **1999**, *189*, 189–204.

- (370) Cerda, B. A.; Wesdemiotis, C. Li^+ , Na^+ , and K^+ binding to the DNA and RNA nucleobases. Bond energies and attachment sites from the dissociation of metal ion-bound heterodimers. *J. Am. Chem. Soc.* **1996**, *118*, 11884–11892.
- (371) Rodgers, M. T.; Armentrout, P. B. Noncovalent Interactions of Nucleic Acid Bases (Uracil, Thymine, and Adenine) with Alkali Metal Ions. Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Am. Chem. Soc.* **2000**, *122*, 8548–8558.
- (372) Yang, Z.; Rodgers, M. T. Tautomerization in the Formation and Collision-Induced Dissociation of Alkali Metal Cation-Cytosine Complexes. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4517–4526.
- (373) Yang, B.; Rodgers, M. T. Alkali Metal Cation Binding Affinities of Cytosine in the Gas Phase: Revisited. *Phys. Chem. Chem. Phys.* **2014**, *16*, 16110–16120.
- (374) Yang, Z.; Rodgers, M. T. Influence of Methylation on the Properties of Uracil and its Noncovalent Interactions with Alkali Metal Ions. Threshold Collision-Induced Dissociation and Theoretical Studies. *Int. J. Mass Spectrom.* **2005**, *241*, 225–242.
- (375) Yang, Z.; Rodgers, M. T. Influence of Halogenation on the Properties of Uracil and Its Noncovalent Interactions with Alkali Metal Ions. Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Am. Chem. Soc.* **2004**, *126*, 16217–16226.
- (376) Yang, Z.; Rodgers, M. T. Influence of Thioketo Substitution on the Properties of Uracil and Its Noncovalent Interactions with Alkali Metal Ions: Threshold Collision-Induced Dissociation and Theoretical Studies. *J. Phys. Chem. A* **2006**, *110*, 1455–1468.
- (377) Ye, S. J.; Moision, R. M.; Armentrout, P. B. Sequential Bond Energies of Water to Sodium Glycine Cation. *Int. J. Mass Spectrom.* **2005**, *240*, 233–248.
- (378) Ye, S. J.; Armentrout, P. B. Guided Ion Beam and Theoretical Studies of Sequential Bond Energies of Water to Sodium Cysteine Cation. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13419–13433.
- (379) Ye, S. J.; Moision, R. M.; Armentrout, P. B. Sequential Bond Energies of Water to Sodium Proline Cation. *Int. J. Mass Spectrom.* **2006**, *253*, 288–304.
- (380) Wincel, H. Hydration energies of sodiated amino acids from gas-phase equilibria determinations. *J. Phys. Chem. A* **2007**, *111*, 5784–5791.
- (381) Wincel, H. Hydration of Potassiated Amino Acids in the Gas Phase. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 2083–2089.
- (382) Wincel, H. Gas-Phase Hydration Thermochemistry of Sodiated and Potassiated Nucleic Acid Bases. *J. Am. Soc. Mass Spectrom.* **2012**, *23*, 1479–1487.
- (383) Wincel, H. Hydration Energies of Protonated and Sodiated Thiouracils. *J. Am. Soc. Mass Spectrom.* **2014**, *25*, 2134–2142.
- (384) Wincel, H. Thermochemistry of Microhydration of Sodiated and Potassiated Monosaccharides. *J. Am. Soc. Mass Spectrom.* **2011**, *22*, 1570–1576.
- (385) Jockusch, R. A.; Lemoff, A. S.; Williams, E. R. Hydration of Valine-Cation Complexes in the Gas Phase: On the Number of Water Molecules Necessary to Form a Zwitterion. *J. Phys. Chem. A* **2001**, *105*, 10929–10942.
- (386) Lemoff, A. S.; Williams, E. R. Binding energies of water to lithiated valine: Formation of solution-phase structure in vacuo. *J. Am. Soc. Mass Spectrom.* **2004**, *15*, 1014–1024.
- (387) Lemoff, A. S.; Bush, M. F.; Williams, E. R. Binding energies of water to sodiated valine and structural isomers in the gas phase: The effect of proton affinity on zwitterion stability. *J. Am. Chem. Soc.* **2003**, *125*, 13576–13584.
- (388) Lemoff, A. S.; Bush, M. F.; Williams, E. R. Structures of Cationized Proline Analogues: Evidence for the Zwitterionic Form. *J. Phys. Chem. A* **2005**, *109*, 1903–1910.
- (389) Lemoff, A. S.; Bush, M. F.; Wu, C.-C.; Williams, E. R. Structures and hydration enthalpies of cationized glutamine and structural analogues in the gas phase. *J. Am. Chem. Soc.* **2005**, *127*, 10276–10286.
- (390) Lemoff, A. S.; Wu, C.-C.; Bush, M. F.; Williams, E. R. Binding energies of water to doubly hydrated cationized glutamine and structural analogues in the gas phase. *J. Phys. Chem. A* **2006**, *110*, 3662–3669.
- (391) Lemoff, A. S.; Bush, M. F.; O'Brien, J. T.; Williams, E. R. Structures of Lithiated Lysine and Structural Analogues in the Gas Phase: Effects of Water and Proton Affinity on Zwitterionic Stability. *J. Phys. Chem. A* **2006**, *110*, 8433–8442.
- (392) Julian, R. R.; Beauchamp, J. L. Site specific sequestering and stabilization of charge in peptides by supramolecular adduct formation with 18-crown-6 ether by way of electrospray ionization. *Int. J. Mass Spectrom.* **2001**, *210–211*, 613–623.
- (393) Ly, T.; Julian, R. R. Using ESI-MS to Probe Protein Structure by Site-Specific Noncovalent Attachment of 18-Crown-6. *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 1209–1215.
- (394) Liu, Z.; Cheng, S.; Gallie, D. R.; Julian, R. R. Exploring the Mechanism of Selective Noncovalent Adduct Protein Probing Mass Spectrometry Utilizing Site-Directed Mutagenesis To Examine Ubiquitin. *Anal. Chem.* **2008**, *80*, 3846–3852.
- (395) Chen, Y.; Rodgers, M. T. Structural and Energetic Effects in the Molecular Recognition of Protonated Peptidomimetic Bases by 18-Crown-6. *J. Am. Chem. Soc.* **2012**, *134*, 2313–2324.
- (396) Chen, Y.; Rodgers, M. T. Re-Evaluation of the Proton Affinity of 18-Crown-6 Using Competitive Threshold Collision-Induced Dissociation Techniques. *Anal. Chem.* **2012**, *84*, 7570–7577.
- (397) Chen, Y.; Rodgers, M. T. Structural and Energetic Effects in the Molecular Recognition of Amino Acids by 18-Crown-6. *J. Am. Chem. Soc.* **2012**, *134*, 5863–5875.
- (398) Chen, Y.; Rodgers, M. T. Structural and Energetic Effects in the Molecular Recognition of Acetylated Amino Acids by 18-Crown-6. *J. Am. Soc. Mass Spectrom.* **2012**, *23*, 2020–2030.
- (399) Yang, B.; Wu, R. R.; Rodgers, M. T. Base-Pairing Energies of Proton-Bound Homodimers Determined by Guided Ion Beam Tandem Mass Spectrometry: Application to Cytosine and 5-Substituted Cytosines. *Anal. Chem.* **2013**, *85*, 11000–11006.
- (400) Yang, B.; Rodgers, M. T. Base-Pairing Energies of Proton-Bound Heterodimers of Cytosine and Modified Cytosines: Implications for the Stability of DNA i-Motif Conformations. *J. Am. Chem. Soc.* **2014**, *136*, 282–290.
- (401) Yang, B.; Moehlig, A. R.; Frieler, C. E.; Rodgers, M. T. Base-Pairing Energies of Protonated Nucleobase Pairs and Proton Affinities of 1-Methylated Cytosines: Model Systems for the Effects of the Sugar Moiety on the Stability of DNA i-Motif Conformations. *J. Phys. Chem. B* **2015**, *119*, 1857–1868.
- (402) Yang, B.; Wu, R. R.; Rodgers, M. T. Base-Pairing Energies of Proton-Bound Dimers and Proton Affinities of 1-Methyl-5-Halocytosines: Implications for the Effects of Halogenation on the Stability of the DNA i-Motif. *J. Am. Soc. Mass Spectrom.* **2015**, *26*, 1469–1482.
- (403) Yang, B.; Rodgers, M. T. Base-Pairing Energies of Protonated Nucleoside Base Pairs of dCyd and m5dCyd: Implications for the Stability of DNA i-Motif Conformations. *J. Am. Soc. Mass Spectrom.* **2015**, *26*, 1394–1403.