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Determination of Metal-Hydroxide Bond Energies in Doubly Charged ScOH, FeOH, and CoOH Ions

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Abstract: Bond dissociation energies of the metal hydroxide dications of Sc, Fe, and Co have been obtained through charge stripping of ions produced by fast atom bombardment. The reactions for fragmentation of the doubly charged transition metal complexes $FeOH^{2+}$ and $CoOH^{2+}$ to produce $M^+ + OH^+$ are exothermic by 0.6 ± 0.5 and 2.2 ± 0.5 eV, respectively. For $ScOH^{2+}$, the corresponding reaction is endothermic by 4.9 ± 0.3 eV. The dissociation reaction to form M^{2+} and the corresponding neutral ligand is endothermic by 4.7 ± 0.3 eV for $ScOH^{2+}$, and by 2.5 ± 0.5 and 1.9 ± 0.5 eV for $FeOH^{2+}$ and $CoOH^{2+}$, respectively.

Studies of coordinatively unsaturated gas-phase metal ions continue to provide insight into the reactivity of both bare and ligated metal centers.[1-17] The great interest in metal ion reactions stems from their relevance to surface chemistry and catalysis, and organometallic and even atmospheric chemistry. Gas-phase metal-ligand bond energies determined by measurements of proton affinities, ionization thresholds, endothermic reaction thresholds, and photodissociation have been used to obtain information about neutral and singly charged metal-ligand species.[18-30] Although there has been recent interest in the chemistry of gas-phase doubly charged metal ions such as Ti^{2+}, Nb^{2+}, Ta^{2+}, La^{2+}, Zr^{2+}, Y^{2+}, and $LaFe^{2+}$,[31-35] there is still relatively little known about the reactivity and thermodynamic properties of gas-phase doubly charged ligated metal ions.[36-38]

Charge stripping has been used extensively to investigate the electronic structure of many organic and inorganic ions.[39-44] The minimum kinetic energy loss, $Q_{\min}$, of the ion M^+ in the charge stripping process (reaction 1, where G is a neutral collision gas,

$$M^+ + G \rightarrow M^{2+} + G + e \qquad (1)$$

usually O_2 or N_2, and e an ejected electron) can be used to determine the second ionization energy of the neutral precursor.

We have previously used charge stripping mass spectrometry (CS) of ions produced by secondary ionization mass spectrometry (SIMS) to investigate effects of ligation on a variety of metal ions.[45] Studies in Gross' laboratory involving the charge stripping investigation of ligated alkaline earth metals have been previously reported.[46] We now show that SIMS/CS can also be used in combination with bond dissociation energies of the monocations available in literature as a novel method for obtaining bond dissociation energies of ligated metal dications. Obtaining the bond dissociation energies for doubly charged metal-ligand

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complexes represents an important step in understanding fundamental properties that influence the chemistry of these species. Only a few examples of bond dissociation energies for dications have been published, including the niobium–carbon bond of $(Nb–CH2)^{2+}$ by Freiser and co-workers[38] and an average ligand binding energies of polyhydrated metal dications $M^{2+}(H_2O)_n$ by Kebarle and co-workers.[47] We illustrate that metal–ligand bond dissociation energies of ScOH, FeOH, and CoOH dications can be obtained by performing charge stripping on the monocation and combining the measured second ionization energies with literature results.

Experimental Section

All mass spectrometric measurements were performed in a VG-Analytical ZAB 2F mass spectrometer with BE geometry. An Ion Tech FAB gun operating at 8 keV with Xe gas was used to produce the secondary ion beam. During the experiment the pressure inside the source was maintained at approximately 10^{-5} mbar.

Samples were obtained by dissolving the appropriate metal salt ($FeCl_3$, $CoCl_2$, and $ScCl_2$) in deionized water. A 2-μL sample of the solution was placed on a stainless steel probe and evacuated in the foreline to remove water from the sample. After the pressure stabilized (3 min), the probe was inserted into position and bombarded with the neutral Xe beam. The mass spectra showed several metal-containing species including metal chlorides (mainly MCl^+ and some MCl_2^+) and metal hydroxides (MOH^+). Metal oxides were not observed in any significant abundances with Fe and Co but were observed for Sc.

Charge stripping was performed by selecting the desired ion with the magnetic sector, colliding the ion with charge stripping gas in the second field free region, and scanning with the electrostatic analyzer the energy ranges containing the precursor ion and the dication energies. The collision gas used was nitrogen (99.999%, Matheson) with indicated pressures typically around 8×10^{-5} mbar. This pressure produced a reduction of 40–50% in the precursor ion beam intensity. This attenuation is estimated to produce an average of less than one collision per ion, although estimates on the number of collisions will vary depending on the instrument, the size of the ions, and the collision gas.[48] Under these conditions a portion of the precursor beam will invariably experience multiple collisions in the collision cell. Multiple collisions can decrease the $Q_{\min}$ value through excitation of the ion to a higher energy state with the first collision and charge stripping from this state with subsequent collisions. However, we find no evidence in the monocation, where second ionization energies are well known, that these processes influence the measurement of the second ionization energies.

Full-scale mass analyzed ion kinetic energy (MIKES) spectra were obtained for all the metal hydroxide monocations. These spectra contain peaks corresponding to the charged stripped dication, MOH^{2+}, as well as MO^+, M^+, OH^+, and M^{2+}, which verify the identity of the monocation precursor. No other peaks above the base-line noise were observed.

The kinetic energy loss, $Q_{\min}$, of the ion was measured by linear graphical extrapolation of the high-energy edge of the parent and the charge stripped peak to the base line. Shown in Figure 1 are the linear extrapolations of the high-energy side of CS peaks for Sc^+ (a), Fe^+ (b), and Co^+ (c). For comparison, the CS analysis of $ScOH^+$ (d) is also shown. Since our data system does not allow extraction of the individual points for analysis, placement of the extrapolating line was performed visually. The uncertainty of this procedure could not be accurately determined but should be reflected in the precision and accuracy (at least for the bare metals) obtained. A method using the centers of Gaussian-fitted curves has been introduced by Caldwell and Gross.[46]

The measurements of the energy shift of the charge stripped peak (as determined by extrapolation) from $E/2$ do not produce $Q_{\min}$ values directly. Several factors including tuning, scan rates, slit widths, instability of the selecting magnet, etc., can shift the relative position of the charge stripped peaks by a few volts. For this reason, a correction factor δ was included to precisely account for the small amounts of kinetic energy shifts. The correction factor was obtained by using a calibrant with a known and well-defined $Q_{\min}$ such as Mg (15.1 eV). For consistency, the charge stripping spectra (calibrant and metal ions) in a given set of experiments were obtained under nearly identical conditions. The value δ was evaluated at the beginning and the end of each determination. Values for δ remained constant (within ±0.2 eV) during this period. For each set of experimental conditions, a new correction factor must be obtained. Typical values for the correction factor δ range between −1.5

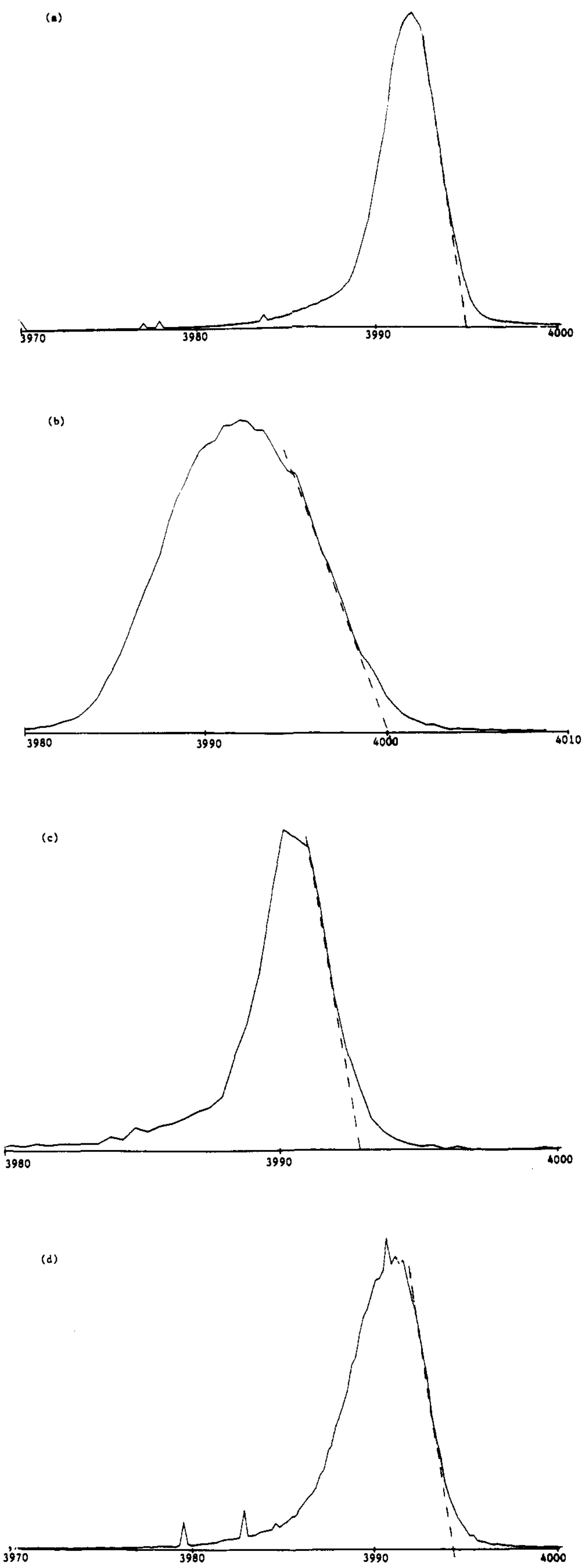

Figure 1. Charge stripping spectra of (a) Sc^+, (b) Fe^+, (c) Co^+, and (d) $ScOH^+$ with N_2 collision gas. Each spectrum was obtained on different days, with the exception of Sc^+ and $ScOH^+$, and under different tuning conditions. Although the resolution varied, for example, between Fe^+ (b) and Co^+ (c), $Q_{\min}$ values were consistent with published second ionization energies for the metals. In general, however, experiments were performed under optimal resolution to minimize the effects of isobaric ions.

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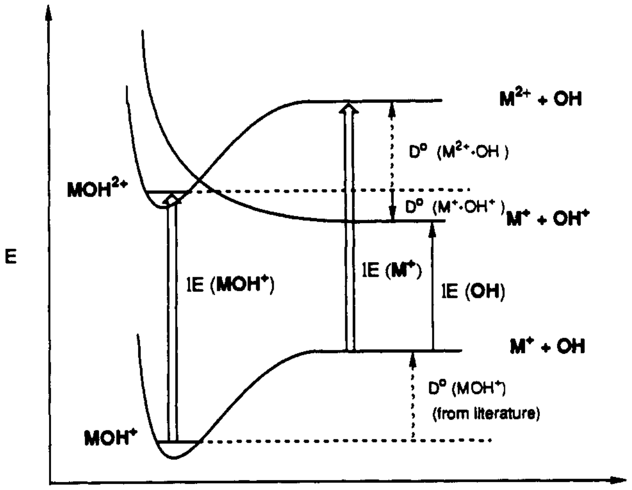
Scheme I. Schematic of the Relationship between Ionization Energies and Bond Dissociation Energies[a]



[a] Relative differences in energy levels are not to scale. No structural information is implied with the relative placement of the energy levels.

and +1.5 eV. For further confirmation, the $Q_{\min}$ value of the bare metal was obtained under identical experimental conditions as the ligated metal ions. This allowed us to determine the overall reliability of the calibration by comparing $Q_{\min}$ values of bare metal ions with published values of their second ionization energies.

For the actual calculation of the $Q_{\min}$, the empirical formula introduced by Ast, Beynon, and co-workers[49] was used, where E_{M^+} is the KE

$$Q_{\min} = E_{M^+} - 2E_{M^{2+}} + \delta \qquad (I)$$

of the parent, $E_{M^{2+}}$ is the KE of the charge stripped peak, and δ is the correction factor determined from the charge stripping of Mg^+. A multiplicative correction method[50] has also been used to obtain $Q_{\min}$ values. The differences between the two methods are discussed elsewhere.[39] In the range of $Q_{\min}$ values obtained in this study, the two methods produce very similar results. However, neither method seems to offer great advantages over the other. We preferred to use the additive method as this is more commonly used.

Bond dissociation energies of the doubly charged ions are obtained using the molecular second ionization energies by the simple thermodynamic relationship shown in Scheme I. No structure is implied with the placement of the respective electronic surfaces. Although organic dications often exhibit exothermic behavior in the fragmentation to two singly charged ions, transition metal complexes can undergo both exothermic and endothermic dissociation. Two dissociation reactions are considered: the loss of a neutral ligand ($OH^•$) and the loss of a singly charged ligand (OH^+), reactions 2 and 3, respectively. The schematic shown below

$$MOH^{2+} \rightarrow M^{2+} + OH^• \qquad (2)$$

applies to the exothermic dissociation to two singly charged species (reaction 3). Equation II provides the dissociation energy of fragmentation

$$D°(M^{2+}\text{–}OH) = D°(M^+\text{–}OH) + IE(M^+) - IE(MOH^+) \qquad (II)$$

to form a doubly charged metal and a neutral ligand (reaction 2), where $D°$ is the bond dissociation energy and IE the ionization energy of the singly charged complex and metal, respectively. For fragmentation to form two singly charged ions (reaction 3), the relationship to obtain the

$$MOH^{2+} \rightarrow M^+ + OH^+ \qquad (3)$$

bond dissociation energy is provided by eq III. In calculating bond

$$D°(M^+\text{–}OH^+) = D°(M^+\text{–}OH) + IE(OH) - IE(MOH^+) \qquad (III)$$

dissociation energies using both eqs II and III, the experimental $Q_{\min}$ values for MOH^+ are used as $IE(MOH^+)$.

For consistency, bond dissociation energies for the transition metal hydroxides (M^+–OH) were obtained from the work of Armentrout and co-workers.[51] It should be noted, however, that similar values for Fe–OH^+ and Co–OH^+ have been published by Freiser and co-workers.[20,28]

Table I. Second Ionization Energies of Bare and Ligated Metals Obtained by Charge Stripping of Singly Charged Ions[a]

	2nd ionization energies/eV		bond dissociation energies/eV		
				dissociation products	
species	$Q_{\min}$ this work	2nd IE lit.	M^+–OH	M^{2+} + OH	M^+ + OH^+
Sc[b]	12.9 ± 0.2	12.80			
Fe[b]	16.3 ± 0.4	16.19			
Co[b]	17.5 ± 0.1	17.08			
ScOH[d]	13.4 ± 0.2	*c*	5.28 ± 0.13	4.7 ± 0.3	4.9 ± 0.3
FeOH[d]	17.0 ± 0.4	*c*	3.35 ± 0.11	2.5 ± 0.5	–0.6 ± 0.5
CoOH[d]	18.4 ± 0.4	*c*	3.18 ± 0.13	1.9 ± 0.5	–2.2 ± 0.5

[a] Bond dissociation energies of metal hydroxide dications are determined using charge stripping mass spectrometry and published thermodynamic data. [b] UV/PES values for second ionization energies from ref 56. [c] Published values are not available. [d] Bond dissociation energies for the corresponding monocations are obtained from ref 51. Earlier similar values are also reported in refs 20 and 28.

A value of 13.01 eV was used for IE(OH).[52]

Results

Second Ionization Energies of Bare and Ligated Metal Ions. The values of the second ionization energies obtained by charge stripping of bare and ligated metal ions are listed in Table I. Several determinations (in parentheses) were used to produce the values tabulated in Table I for Sc^+ (3), Fe^+ (4), Co^+ (4), $ScOH^+$ (3), $FeOH^+$ (3), and $CoOH^+$ (4). The uncertainties expressed correspond to one standard deviation unit for the group of measurements of a given species. The selection of the extrapolation line is probably the major contributor to the deviation in the $Q_{\min}$ values. For spectra with large signal to noise, selecting the extrapolation line is straightforward. However, for spectra with low signal to noise, several extrapolation lines are possible providing slightly varying $Q_{\min}$ values. For the species reported here, the signal to noise was not a problem, and selection of the extrapolation line could be performed with certainty. The linear correction factor could also introduce uncertainties in the $Q_{\min}$ values, but the effects would be more systematic than random. It has not been established, however, whether a linear or a multiplicative correction factor produces more precise and accurate results. We therefore chose both linear correction factor and linear extrapolation methods since most charge stripping experiments have already been performed using these two methods. It is, however, clear that further investigations on the nature of charge stripping must be performed to obtain more accurate values for second ionization energies. In any case, the precision of the measurements generally produce deviations of less than ±0.4 eV. This value is consistent with other values for uncertainties reported for charge stripping.[41,43,44,49,50] Caldwell and Gross have reported higher precision (±0.1 eV) which could be attributed to the Gaussian-fit method they propose and/or the high cross sections for charge stripping of the alkali earth metal complexes they studied.[46]

For the transition metals other sources of error may be attributable to low-lying excited states of the precursor ions. For atomic ions these would be electronic states, and for ionic molecules it may be a combination of excited electronic and vibrational states. The $Q_{\min}$ values reported here for the three transition metal ions, along with those obtained earlier for other transition, rare earth, and alkaline earth metal ions we have charge stripped, agree to within ±0.5 eV of literature values for the second IE's obtained by UV/photoelectron spectroscopy (UV/PES).[45,53] This value for the uncertainty actually represents the largest deviation, with the average deviation being ±0.3 eV. The bare metal ion spectra contain no peaks between $E/2$ and the onset of the charge stripping peak that would indicate the presence of long-lived excited states with energies greater than at least 0.5 eV of the ground state.

The presence of excited states would decrease the $Q_{\min}$ values relative to UV/PES values. However, the $Q_{\min}$ values reported here are generally greater than values obtained by UV/PES

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methods. For example, the average Q_{min} value is 0.1 eV greater than the UV/PES value for Fe^+ and 0.4 eV greater for Co^+. The lowest electronically excited states for these two ions have energies of 0.25 eV and 0.41 eV, respectively, above the ground state. In any case, these differences are below or near the precision of the technique and may not be readily observed. The value of Sc^+ (12.9 eV) also closely agrees with the UV/PES value (12.8 eV). The first excited state of Sc^+ is only 0.32 eV greater than the ground state. The difference in energy between the two states is again below the precision of the method and may not be easily observed.

The Q_{min} values of metal hydroxides are generally larger than the bare metal ions. This trend is consistent with simple electronegativity considerations as our group and Caldwell and Gross have previously reported.[45,46] Interestingly, differences in Q_{min} values between M^+ and MOH^+ fall within a narrow range, 0.5 eV (Sc), 0.7 eV (Fe), and 0.9 eV (Co^+). Larger differences in Q_{min} values between bare and ligated metal ions are generally observed with more electronegative ligands (such as O and Cl) and larger metal atoms.[45,53]

The precision of the Q_{min} values for the ligated metal ions do not differ from the bare metal ions. However, the determinations of Q_{min} values for molecular ions could be complicated by additional factors: vibrational (and rotational) excitation and the presence of isobaric ions. As with many ionization methods, the degree of vibrational and rotational excitation during FAB ionization has not been well characterized, and no satisfactory method exists at this time to determine the extent of excitation in these systems. The Q_{min} values obtained by extrapolating the high-energy side of the peak to the base line will be affected if vibrational and rotational excitation are sufficient to vary the slope. Any amount of excitation will produce Q_{min} values which are lower than the true second ionization energies. Large deviations, i.e., several electron volts, should not be observed since highly vibrationally excited molecules will simply fall apart and will not be detected. Nonetheless, the reported values should be accepted only as lower limits for second ionization energies. These uncertainties will naturally be reflected in the measured bond dissociation energies as discussed below. Inspection of the relative slopes of the extrapolation show deviation of less than 5% between the bare and ligated metal ions. This corresponds to differences in the Q_{min} values which are less than the average deviation of measured Q_{min} values for a given molecule. In any case, the change in the slope may not only be caused by excited ions but differences in collision rates and the collection profile of the scattered beam. It will be useful, in the future, to develop a molecular ion as reference in conjunction with SIMS for the charge stripping of metal containing molecular ions.

The presence of isotopic peaks can also be problematic. For example, the signal corresponding to m/z 73 for $^{56}FeOH^+$ contains some amount of $^{57}FeO^+$. Fortunately, this amount is less than 1% as estimated from the presence of ^{56}FeO (<5%) and the natural abundance of ^{57}Fe (2.2%). In greater abundances, it could affect the determination of the Q_{min} if its reaction cross section for charge stripping is significantly greater than the corresponding hydroxide and its Q_{min} value is lower than that of the hydroxide. Depending on the interfering ion's abundance, it could appear as a very small shoulder (or bump) on the high-energy side of the CS peak of the hydroxide. Both Co and Sc are monoisotopic and do not have interfering isobaric species for the metal hydroxide.

Bond Dissociation Energies of Doubly Charged Ions. The thermicity of the dissociation varies greatly between the two fragmentation processes. Reactions involving formation of doubly charged metal ions (reaction 2) are in all cases endothermic by 4.7 eV ($ScOH^{2+}$), 1.9 eV ($CoOH^{2+}$), and 2.5 eV ($FeOH^{2+}$). The dissociation process to form two singly charged species (reaction 3) is 2.2 eV exothermic for $CoOH^{2+}$, only 0.6 eV exothermic for $FeOH^{2+}$, and endothermic by 4.9 eV for $ScOH^{2+}$. Owing to the uncertainty of the method, it is possible that the dissociation of $FeOH^{2+}$ to form two singly charged ions is essentially a thermoneutral process.

The behavior of $FeOH^{2+}$ and $ScOH^{2+}$ contrasts with the observation that the dissociation of dications to form two monocations is often a highly exothermic process. An extreme example is that of the dihelium dication, which has an exothermicity for fragmentation to two singly charged helium ions of nearly 9 eV. Observation of the doubly charged species can be explained by the large barrier to dissociation, which for $He_2{}^{2+}$ is approximately 1.5 eV,[54] and, in fact, $He_2{}^{2+}$ has been observed using chemical ionization CS mass spectrometry.[55]

For $ScOH^{2+}$ the two processes converge; i.e., the energetics to produce the doubly charged metal and neutral ligand and to form the singly charged metal and ligand are similar. The dissociation energy associated with reaction 2 for $ScOH^{2+}$ is nearly twice that of either $CoOH^{2+}$ and $FeOH^{2+}$. A similar situation arises in the dissociation via reaction 3. In this case, both $FeOH^{2+}$ and $CoOH^{2+}$ undergo exothermic reactions while $ScOH^{2+}$ dissociation is highly endothermic. Thus, in the dication as in the monocation, there is a large difference between early and mid to late transition metals in terms of bond dissociation energies.

Sources of error in these calculations come from the charge stripping process, the respective first and second ionization energies of the ligand and bare metal (UV/PES), and the bond dissociation energies for the corresponding singly charged ion. Charge stripping and the bond dissociation energies for the singly charged species, however, account for the largest error in the determination of bond dissociation energies. Typical deviations within the UV/PES data are less than 0.01 eV, while uncertainties in the bond energies for the singly charged complexes are less than 0.3 eV. In the charge stripping of molecular ions, experimental error can come from the excited (vibrational and electronic) states populated by the precursor ion. The Q_{min} of an excited-state species is lower than the true second ionization value. This would increase the relative energy of the doubly charged species which, in turn, would decrease the calculated energy for endothermic processes. Thus, in the presence of excited states, endothermic dissociation reactions, e.g., the energy associated with reaction 2, would be over estimated. The values reported here would then be the upper limit for bond dissociation energies of endothermic processes. Conversely, the energy associated with the exothermic processes would be underestimated so that the corresponding values would be the minimum or lower limit of the bond dissociation energies.

We believe the SIMS/CS method in conjunction with published literature values can be a useful method for estimating bond dissociation energies of doubly charged metal ions coordinated to a single ligand. The advantage of charge stripping of SIMS produced ions is that the bond dissociation energies of theoretically interesting but previously inaccessible species can be obtained. The effects of vibrational excitation will be investigated in future work by producing ions in the source using ion/molecule reactions and by collisionally cooling SIMS produced ions in the source. Theoretical studies are also underway to compare the values obtained experimentally with those calculated by ab initio methods.

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