

# Threshold Collision-Induced Dissociation Determination and Molecular Orbital Calculations of the Binding Energies of Sodium and Silver Ions to Small Nitrogen-Containing Ligands

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The binding energies at 0 K of sodium and silver ions to ammonia, methylamine, ethylamine, acetonitrile, and benzonitrile were determined using threshold collision-induced dissociation (CID) and molecular orbital calculations at the ab initio and density functional theory levels. There is good agreement between experimental and calculated binding energies. For the five ligands, threshold CID/CCSD(t)(fu)/6-311++G(2df,p)//MP2-(fu)/6-311++G(d,p) Na<sup>+</sup> binding energies are the following: ammonia, 25.6 ± 2.8/24.8; methylamine, 27.0 ± 1.4/25.9; ethylamine, 27.7 ± 2.3/27.1; acetonitrile, 30.0 ± 2.3/30.3; and benzonitrile, 32.7 ± 1.4/35.0 (B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)) kcal/mol. Threshold CID and B3LYP/DZVP Ag<sup>+</sup> binding energies are the following: ammonia, 40.6 ± 3.0/38.9; methylamine, 41.5 ± 2.3/41.1; ethylamine, 42.9 ± 1.4/43.2; acetonitrile, 40.8 ± 2.0/39.3; and benzonitrile, 41.5 ± 2.8/43.1 kcal/mol. Wherever comparisons with literature data are possible, the Na<sup>+</sup> binding energies determined in this study are in good agreement with established data. For Ag<sup>+</sup> binding energies, agreement with the few published theoretical values is not as good. A comparison of Na<sup>+</sup> and Ag<sup>+</sup> binding energies for the five N-containing ligands in this study and those for water, methanol, and ethanol published earlier (El Aribi, H.; Shoeib, T.; Ling, Y.; Rodriquez, C. F.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. A* 2002, 106, 2908–2914) shows that for every ligand the Ag<sup>+</sup> binding energy is higher than the Na<sup>+</sup> binding energy. As a group, the amines exhibit the largest differences between Ag<sup>+</sup> and Na<sup>+</sup> binding energies, followed by the nitriles; the alcohols exhibit the smallest differences. These results are in line with previous observations that Ag<sup>+</sup> prefers binding with nitrogen to binding with oxygen.

## Introduction

Metal ions are essential to life. They play diverse roles in biology.<sup>1–3</sup> Alkali metal ions such as Na<sup>+</sup> and K<sup>+</sup> are important charge carriers and are responsible for osmotic balance in a cell. Alkaline earth metal ions, for example, Mg<sup>2+</sup> and Ca<sup>2+</sup>, are integral parts of proteins and are essential to their functions. Some ionophores (e.g., monensin A) display remarkable selectivity for Na<sup>+</sup>, whereas others (e.g., nonactin) are selective for K<sup>+</sup>. Polypeptides such as gramicidin A form ion channels through which Na<sup>+</sup> can be transported.<sup>1–3</sup> The Ag<sup>+</sup> ion has long been used as a bactericide in newborns;<sup>4,5</sup> some silver complexes have been found to have remarkable antimicrobial activities.<sup>6,7</sup> The silver ion binds very tightly to metallothioneins, a class of small proteins believed to be involved in metal transport as well as detoxification.<sup>8–10</sup>

The binding energy between a metal ion, M<sup>+</sup>, and a ligand, L, is defined as the enthalpy change, ΔH<sup>o</sup><sub>T</sub>, of the following dissociation reaction at temperature T, which is almost always at 0 K:



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The binding energies of Na<sup>+</sup> are, perhaps, the most extensively known among all metal ion binding energies.<sup>11–23</sup> Experimental techniques that have successfully been used to measure Na<sup>+</sup> binding energies include high-pressure mass spectrometry (HPMS),<sup>11,16–19</sup> threshold collision-induced dissociation (CID),<sup>13,14,20–23</sup> and Fourier transform ion cyclotron resonance (FTICR).<sup>12</sup> Many theoretical methods have also been applied to calculate Na<sup>+</sup> binding energies.<sup>13,15,22,23</sup> In contrast, the binding energies of Ag<sup>+</sup> are among the least known, despite recent interest in the binding chemistry of Ag<sup>+</sup> to amino acids and peptides<sup>24–39</sup> and in employing argentinated peptides for sequencing.<sup>24,27,34</sup> HPMS,<sup>40</sup> threshold CID,<sup>23,41</sup> and FTICR<sup>42</sup> methods have all been employed, but the number of studies and the ligands covered are comparatively limited. Theoretical treatment of Ag<sup>+</sup> binding is almost as sparse;<sup>23,28–33,41–46</sup> a reason for this may be the very limited availability of basis sets for silver.

Very recently, we reported experimental and theoretical Ag<sup>+</sup> binding energies of a number of small oxygen-containing ligands.<sup>23</sup> Measurements were performed by means of the threshold CID technique<sup>13,14,20–23,41</sup> while calculations were carried out using density functional theory (DFT) via the hybrid B3LYP method<sup>47–49</sup> in combination with a double-zeta valence-polarization (DZVP) basis set<sup>50,51</sup> developed for DFT. Because our threshold CID experiments were performed on a commercially available triple-quadrupole mass spectrometer, as opposed to a well-tested guided ion-beam system, we also

decided to measure the Na<sup>+</sup> binding energies of a number of the O-containing ligands as well as calculate them using coupled-cluster and DFT methods to validate our experimental protocol. There was good agreement between our experimental and theoretical Na<sup>+</sup> binding energies and acceptable to good agreement between our data and literature data. The Ag<sup>+</sup> binding energy is consistently larger than the corresponding Na<sup>+</sup> binding energy for every ligand in which both binding energies were available.<sup>23</sup>

Here we report threshold CID and calculated binding energies of Na<sup>+</sup> and Ag<sup>+</sup> for a number of nitrogen-containing ligands: ammonia, methylamine, ethylamine, acetonitrile, and benzonitrile. The first three ligands mimic the amino functional group on the N-terminus in peptides as well as that on the side chain of lysine residues; metal ion binding to the last two ligands (the nitriles) has attracted much recent interest.<sup>19,22,41</sup> The relative binding strengths of Na<sup>+</sup> and Ag<sup>+</sup> to these nitrogen-containing ligands as well as to the oxygen-containing ligands examined earlier<sup>23</sup> will be compared.

### Experimental Method and Data Treatment

The experimental details and information on the full data treatment have been reported elsewhere.<sup>23</sup> Below is a summary of the key features. Threshold CID measurements were conducted on a PE SCIEX API III triple-quadrupole mass spectrometer (Concord, Ontario, Canada). Samples were typically 50 μM in ligand and 30 μM in silver nitrate in solutions of 50:50 water/methanol. They were electrosprayed at a typical flow rate of 2 μL/min with air being the nebulizer gas. Ions thus formed were sampled from the atmospheric pressure ion source into an “enclosed” quadrupolar lens region (q0), where multiple collisions with the “curtain-gas” molecules of nitrogen sampled with the ions occur. The bias potentials in this lens region were selected to optimize between adequate transmission and minimal collisional heating of the silver–ligand complex. Extensive studies have shown that thermalization of the sampled ions from the orifice to the lens region is highly efficient.<sup>52–59</sup> Collision-induced dissociation was performed using argon as the neutral gas; in our hands, the performance of Ar and Xe were comparable.<sup>23</sup> The gas pressure in q2 was continuously monitored with an upstream baratron gauge, the read out of which was converted into collision-gas thickness values (CGT, the product of the neutral-gas number density and the length of q2)<sup>60</sup> by the mass spectrometric software.

The threshold energy for the CID of a given M<sup>+</sup>–L complex was determined using the curve-fitting and modeling program CRUNCH developed by Armentrout and co-workers.<sup>61–67</sup>

$$\sigma(E) = \sigma_0 \sum g_i (E + E_i - E_0)^n / E \quad (2)$$

where  $\sigma(E)$  is the dissociation cross section,  $\sigma_0$  is a scaling factor,  $E$  is the center-of-mass collision energy ( $E_{\text{cm}}$ ),  $E_0$  is the threshold energy,  $E_i$  is the internal energy of a given vibrational state with a relative population  $g_i$ , and  $n$  is an adjustable parameter. An inherent assumption in the use of eq 2 is that a precursor ion with an internal energy greater than  $E_0$  will fragment to form the product ion in q2. With increasing complexity of the precursor ion, there is an increasing probability that the fragmentation reaction will not occur within the precursor ion's residence time in q2. For a relatively large precursor ion that has many degrees of freedom, additional internal energy may be needed to increase the fragmentation rate to a magnitude that the dissociation in q2 becomes measurable. This additional internal energy, the kinetic shift, must be subtracted from the apparent threshold to yield the true

$E_0$ . The magnitude of this additional energy can be estimated from the unimolecular rate constant of the dissociation according to the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.<sup>68–70</sup> When this is done, eq 2 is modified to become

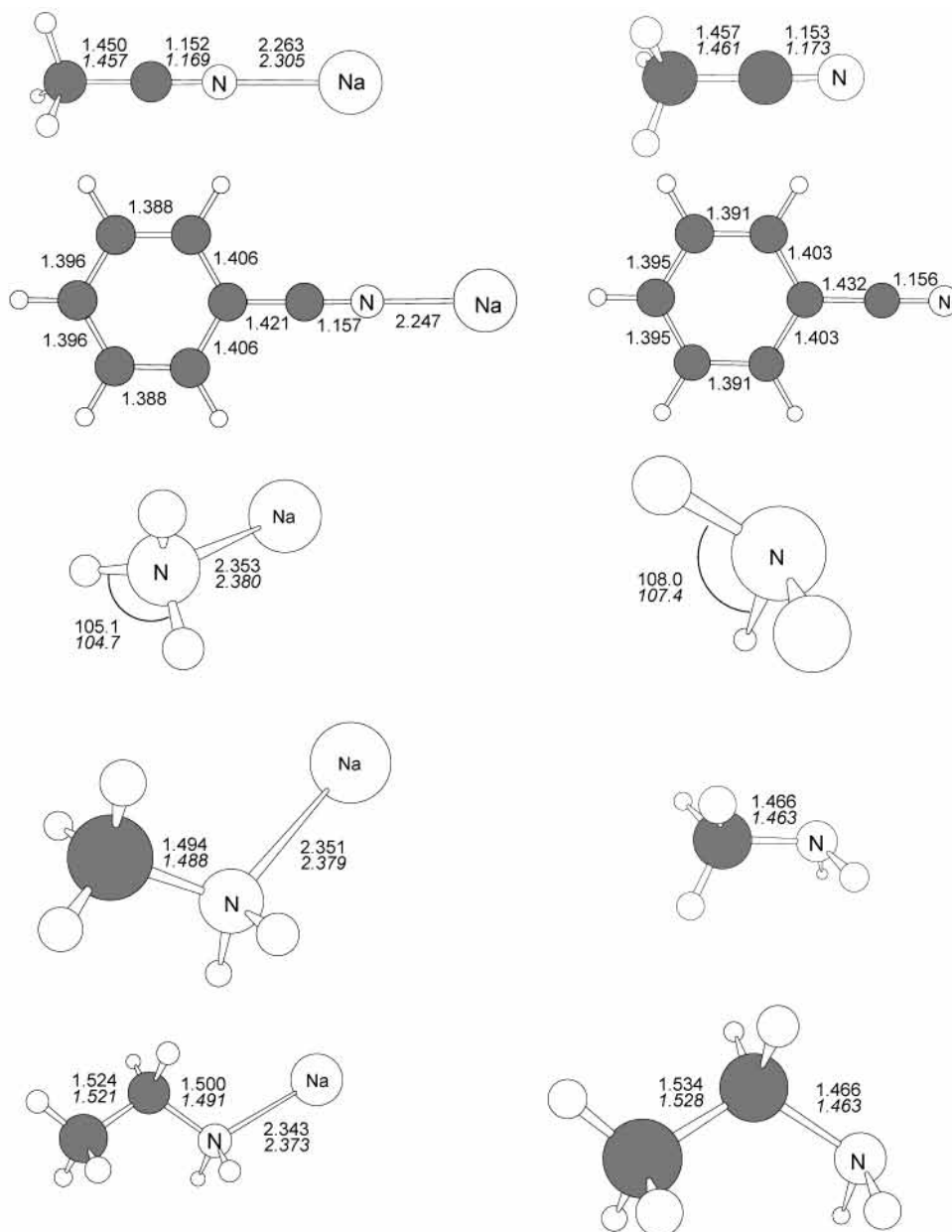
$$\sigma(E) = \sigma_0 \sum g_i P(E, E_i, t) (E + E_i - E_0)^n / E \quad (3)$$

where  $P$  is the probability that a precursor ion of collision energy  $E$  and internal energy  $E_i$  will fragment within a residence time  $t$ . The residence time of a given precursor ion was estimated using a procedure similar to that of Klassen and Kebarle.<sup>71</sup> In our apparatus, ion residence times for the Na<sup>+</sup>–L complexes were found to range from 30 to 42 μs, and those for the Ag<sup>+</sup>–L complexes, from 25 to 30 μs. These values are comparable to those reported earlier<sup>23</sup> and are very similar to those of Kebarle and co-workers.<sup>71,72</sup>

Determination of  $E_0$  requires the vibrational frequencies and rotational constants of the precursor ions and the transition states. These transition states were assumed to be loose and product-like (the phase-space limit, PSL), and their vibrational frequencies were approximated by those of the neutral products obtained in the ab initio and DFT calculations (see Table 1s). The vibrational modes of the precursor ion that became rotations of the completely dissociated products were treated as rotors. The transition state was assumed to be variationally located at the centrifugal barrier, and the adiabatic 2D rotational energy was calculated according to the statistical average approach of Rodgers et al.<sup>66</sup> In Results and Discussion, it will be shown that the  $E_0$  values for ammonia, methylamine, ethylamine, and acetonitrile obtained with and without the kinetic shift consideration are comparable (i.e., the kinetic shifts are insignificant), thus rendering the details of the choice for the transition states and vibrational frequencies relatively unimportant. Even for benzonitrile, the largest ligand, the kinetic shift amounts to only 9 and 16% of the PSL  $E_0$  values for its sodium and silver ion complexes, respectively.

The dissociation cross sections of the product ions, Na<sup>+</sup> and Ag<sup>+</sup>, were determined as a function of the center-of-mass energies at four argon pressures, typically at CGT values of  $100 \times 10^{12}$ ,  $70 \times 10^{12}$ ,  $50 \times 10^{12}$ , and  $30 \times 10^{12}$  atoms cm<sup>-2</sup>. For an ion that has a collision cross section of  $100 \text{ \AA}^2$ , it will have, on average, one collision in q2 with argon having a CGT value of  $100 \times 10^{12}$  atoms cm<sup>-2</sup>. To eliminate the effects of multiple collisions,  $E_0$  values were obtained from threshold curves constructed only from  $\sigma(E)$  at zero CGT. These cross sections were obtained by extrapolating the  $\sigma(E)$  versus CGT function to zero CGT via the least-squares fit of the presumed exponential function.<sup>23</sup> Typically, a threshold curve comprises 120  $\sigma(E)$  values over an  $E_{\text{cm}}$  range of 0–4 eV.

Evaluation of  $E_0$  took into account of the ion energy distribution<sup>73</sup> and the thermal motion of argon.<sup>73,74</sup> These details have been discussed elsewhere.<sup>14,23</sup> As before, uncertainties in the binding energies measured in replicate analyses were comparable to the difference in the means determined at the two possible extreme argon temperatures of 20 and 298 K; as a result, the binding energies reported herein are averages, and the uncertainties are the combined uncertainties of the data sets. Ion energy distributions of approximately 2 eV (full width at half-maximum) in the laboratory frame were observed for all ion complexes. These values are practically identical to those observed in an earlier study and are comparable to the best results seen on similar instrumentation.<sup>71,72</sup> As shown earlier, the ion temperature is not a sensitive parameter in the modeling; although we are assuming an ion temperature of 298 K, varying the ion temperature by approximately  $\pm 100$  K results in a



**Figure 1.** Minimum structures of the ligands and their sodiated complexes. ●, C; ○, H; N and Na are labeled. Bond distances are in Å; italicized numbers are from MP2(fu)/6-311++G(d,p) calculations; and nonitalicized numbers are from B3LYP/6-311++G(d,p) calculations.

change in the  $E_0$  value that is typically  $<3$  kcal/mol, a value comparable to the stated uncertainties of 2–3 kcal/mol for  $E_0$ .<sup>23</sup>

### Computational Methods

Ab initio and DFT calculations were employed using Gaussian 98.<sup>75</sup> For sodiated complexes and their ligands, geometric optimizations were first performed at the MP2(fu)/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory, followed by single-point calculations using CCSD(t)(fu)/6-311++G(2df,p) at the optimized MP2 and B3LYP geometries. For argentinated complexes and ligands, all calculations were performed using B3LYP/DZVP. The DZVP basis set has previously been found to work well for  $\text{Ag}^+$ -containing complexes.<sup>23,28–33,41,45</sup>

The binding energy between  $\text{M}^+$  and L, the standard enthalpy change of the reaction  $\text{M}^+ - \text{L} \rightarrow \text{M}^+ + \text{L}$  at 0 K,  $\Delta H^{\circ}_0$ , was calculated as follows:

$$\Delta H^{\circ}_0 = \Delta E_{\text{elec}} + \Delta E_{\text{ZPVE}} \quad (4)$$

$\Delta E_{\text{elec}}$  and  $\Delta E_{\text{ZPVE}}$  are the changes in electronic energies and zero-point vibrational energies, respectively, between the products and the reactant in the dissociation reaction. Basis set superposition errors (BSSEs) were evaluated using the full counterpoise procedure<sup>76</sup> and were subtracted from the uncorrected binding energies.

### Results and Discussion

**Ligand and Complex Structures and Energetics. Sodiated Complexes.** Table 1 shows the electronic energies, zero-point vibrational energies, thermal corrections ( $H^{\circ}_{298} - H^{\circ}_0$ ), and entropies of the five N-containing ligands—ammonia, methylamine, ethylamine, acetonitrile, and benzonitrile—and their sodiated complexes from B3LYP/6-311++G(d,p) calculations. Vibrational frequencies and rotational constants were used in the  $E_0$  determinations; these values are listed in Table 1s in Supporting Information. The optimum MP2 and B3LYP geometries of the ligands and their sodiated complexes are illustrated in Figure 1. Bond distances in italics are those from

**TABLE 1: Electronic Energies, Zero-Point Vibrational Energies (ZPVE), Thermal Energies, and Entropies of the Ligands and Their Na<sup>+</sup> Complexes from B3LYP/6-311++G(d,p) Calculations**

species	electronic energy hartrees	ZPVE kcal/mol	$H_{298}^{\circ} - H_{0}^{\circ}$ kcal/mol	entropy cal/(K mol)
ammonia	-56.58272	21.5	2.4	48.0
methylamine	-95.89389	40.0	2.8	57.5
ethylamine	-135.22152	57.9	3.4	65.1
acetonitrile	-132.79620	28.3	2.9	60.1
benzonitrile	-324.57783	62.0	4.4	78.5
Na <sup>+</sup> -ammonia	-218.71702	23.5	3.0	60.4
Na <sup>+</sup> -methylamine	-258.02908	41.6	3.7	69.4
Na <sup>+</sup> -ethylamine	-297.35857	59.4	4.4	76.9
Na <sup>+</sup> -acetonitrile	-294.93697	29.1	4.0	72.6
Na <sup>+</sup> -benzonitrile	-486.72231	62.8	5.7	91.1
Na <sup>+</sup>	-162.08757		1.5	35.3

<sup>a</sup> Sum of translational, vibrational, and rotational energies required to convert between 0 and 298 K.

**TABLE 2: Threshold Binding Energies of Na<sup>+</sup> to Ligands**

ligand	$E_0$ eV	$E_0$ (PSL) eV	$\Delta S^{\ddagger}$ (PSL) <sup>a</sup> cal/(K mol)
ammonia	1.11 ± 0.12	1.11 ± 0.12	8.46
methylamine	1.17 ± 0.06	1.17 ± 0.06	9.14
ethylamine	1.20 ± 0.10	1.20 ± 0.10	8.08
acetonitrile	1.30 ± 0.10	1.30 ± 0.10	4.05
benzonitrile	1.55 ± 0.06	1.42 ± 0.06	5.54

<sup>a</sup> Entropy of activation at 1000 K.

MP2 calculations. It is readily apparent that the geometries obtained from the two methods are virtually identical. Binding of Na<sup>+</sup> occurs in every case at the nitrogen atom and with minimal perturbation to the ligand structure. The Na<sup>+</sup>-N bond distance increases from a minimum of 2.247 Å in sodiated benzonitrile to a maximum of 2.353 Å (B3LYP calculation) in sodiated ammonia. The trend of increasing Na<sup>+</sup>-N bond distance in sodiated complexes in the series benzonitrile < acetonitrile < ethylamine < methylamine < ammonia is consistent with the trend of decreasing sodium ion binding

energies in benzonitrile > acetonitrile > ethylamine > methylamine > ammonia (vide infra).

The  $E_0$  values of the five sodiated complexes are shown in Table 2. Two types of  $E_0$  data are on display: those obtained without consideration of dissociation rates (i.e., no kinetic shifts are assumed and the data are labeled simply as  $E_0$ ) and those for which kinetic shifts are taken into account (labeled as  $E_0$ - (PSL)). It is apparent that the kinetic shift is significant only for sodiated benzonitrile, the largest complex. The  $E_0$ (PSL) values have been converted to Na<sup>+</sup> binding energies in Table 3, which also shows the calculated sodium binding energies of the five ligands, the BSSE corrections (which have already been factored into the displayed binding energies), and literature binding energies. Our calculations show that, in four of the five cases for which both MP2 and B3LYP geometric optimizations were carried out, the B3LYP binding energies are higher by approximately 2 kcal/mol. Coupled-cluster single-point calculations yield practically identical binding energies from MP2- and B3LYP-optimized structures. There is good to excellent agreement between our theoretical data and the recent data of Petrie,<sup>15</sup> who employed more computationally intensive composite techniques, and the theoretical data of Armentrout et al.<sup>13</sup> and Valina et al.<sup>22</sup> The trend of higher binding energies from B3LYP than from MP2 is also apparent in the data of the last two groups.<sup>13,22</sup>

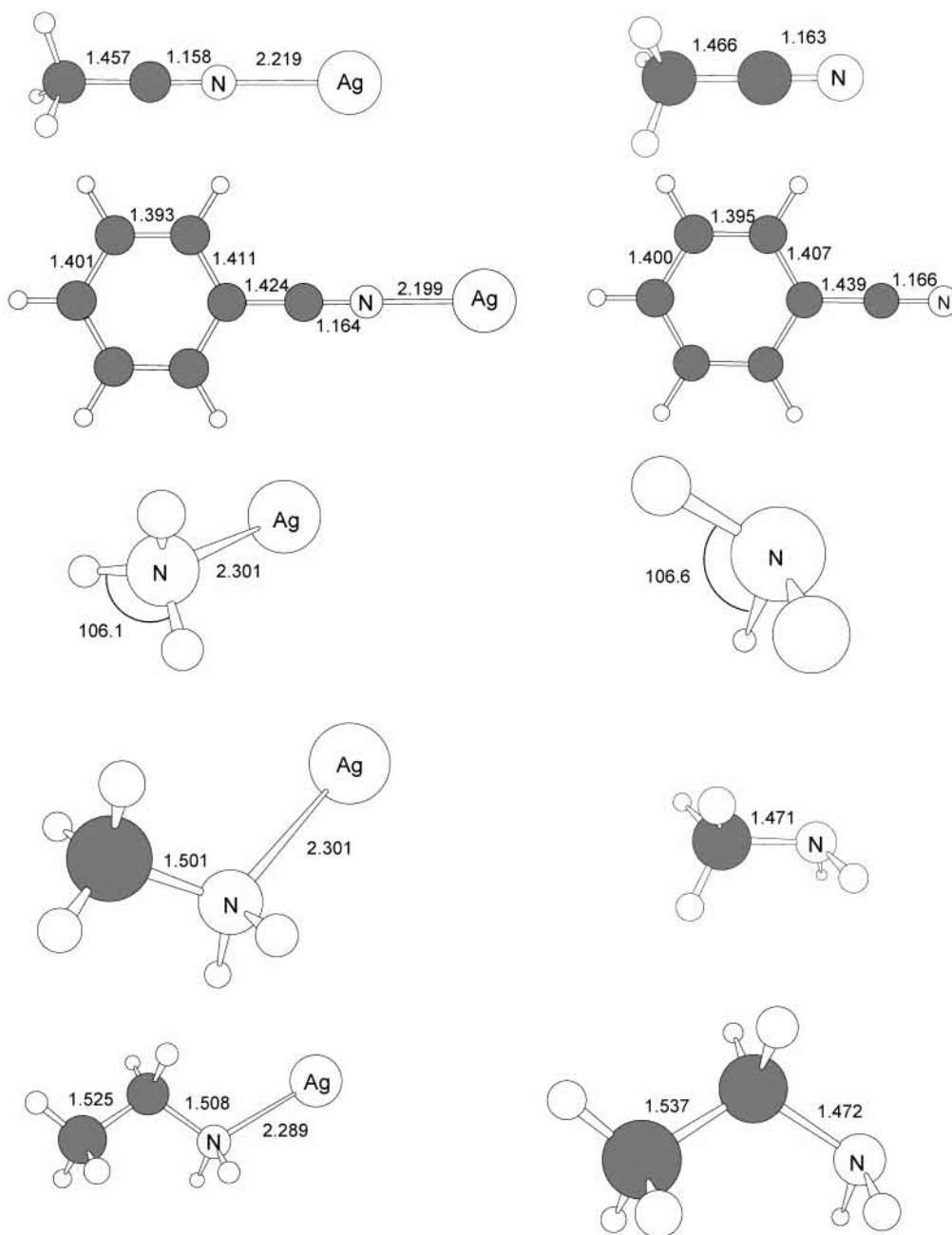
The threshold CID-determined binding energies obtained in this study are in good agreement with the theoretical binding energies. The experimental uncertainties in the range of ±1.3 to ±2.8 kcal/mol are comparable to the expected accuracies of 2–3 kcal/mol in our ab initio and DFT calculations, which have repeatedly been observed when calculated binding energies at these levels of theory were rated against the best experimental data.<sup>76,77</sup> The differences between the theoretical binding energies and the experimental Na<sup>+</sup> binding energies are all smaller than ±3 kcal/mol. For ammonia and acetonitrile, two cases in which comparisons of threshold CID data are possible, our values are in good agreement with those of Armentrout et

**TABLE 3: Binding Energies of Na<sup>+</sup> to Ligands at 0 K<sup>a</sup> (kcal/mol)**

ligand	ammonia	methylamine	ethylamine	acetonitrile	benzonitrile
this study					
threshold CID	25.6 ± 2.8	27.0 ± 1.4	27.7 ± 2.3	30.0 ± 2.3	32.7 ± 1.4
MP2 <sup>b</sup>	24.5 (2.0) <sup>c</sup>	25.6 (1.8)	26.8 (1.8)	29.2 (1.1)	
CCSD(t)(fu) <sup>d</sup>	24.8 (1.9)	25.9 (1.9)	27.1 (2.0)	30.3 (1.6)	
B3LYP <sup>e</sup>	26.4 (0.9)	27.5 (0.8)	28.8 (0.7)	32.3 (0.3)	35.0 (0.4)
CCSD(t)(fu) <sup>f</sup>	25.2 (1.5)	25.9 (1.9)	27.3 (1.9)	30.2 (1.7)	
Armentrout et al. <sup>g</sup>					
threshold CID	24.4 ± 1.3				
MP2	24.5	26.0			
B3LYP	26.0	27.6			
Valina et al. <sup>h</sup>					
threshold CID				30.5 ± 1.1	
MP2				30.0	
B3LYP				32.5	
McMahon et al. <sup>i</sup>	24.5 ± 0.4	25.8 ± 0.2	27.3 ± 0.4	29.9 ± 0.4	
Hoyau et al. <sup>j</sup>	24.7 ± 0.2	25.7 ± 0.2			
Petrie <sup>k</sup>	25.0/25.2	26.6/26.8	27.7	30.7	
Castleman et al. <sup>l</sup>	28.2 ± 0.4				
Marinelli et al. <sup>m</sup>	27.5 ± 4.3				
Davidson et al. <sup>n</sup>			31		

<sup>a</sup> Literature values not at 0 K have been converted to that temperature. <sup>b</sup> MP2(fu)/6-311++G(d,p)//MP2(fu)/6-311++G(d,p). <sup>c</sup> BSSE correction, which has been incorporated into the displayed binding energy. <sup>d</sup> CCSD(t)(fu)/6-311++G(2df,p)//MP2(fu)/6-311++G(d,p). <sup>e</sup> B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p). <sup>f</sup> CCSD(t)(fu)/6-311++G(2df,p)//B3LYP/6-311++G(d,p). <sup>g</sup> Reference 13; MP2 = MP2(fu)/6-311+G(2d,2p)//MP2(fu)/6-31G(d); and B3LYP = B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d). <sup>h</sup> Reference 22; MP2 = MP2(fu)/6-311+G(2d,2p)//MP2(fu)/6-31G(d); and B3LYP = B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d). <sup>i</sup> Reference 12; binding energies are those converted from  $\Delta G_{298}^{\circ}$  values by Petrie.<sup>15</sup> <sup>j</sup> Reference 11; converted from  $\Delta H_{298}^{\circ}$  values using thermal corrections in this study. <sup>k</sup> Reference 15; CPd-G2thaw/c-SLW3; the latter level is available only for ammonia and methylamine. <sup>l</sup> Reference 17. <sup>m</sup> Reference 20. <sup>n</sup> Reference 19.





**Figure 2.** Minimum structures of the ligands and their argentinated complexes. ●, C; ○, H; N and Ag are labeled. Bond distances from B3LYP/DZVP calculations are in Å.

al.,<sup>13</sup> Marinelli and Squires,<sup>20</sup> and Valina et al.<sup>22</sup> For ammonia, methylamine, ethylamine, and acetonitrile, the agreement between our threshold CID data and the FTICR data of McMahon and Ohanessian<sup>12</sup> is equally good. Good agreement is also evident between our data and the HPMS data of Hoyau et al.<sup>11</sup> and Davidson and Kebarle.<sup>19</sup>

**Argentinated Complexes.** Table 4 shows the electronic energies, zero-point vibrational energies, thermal corrections ( $H^{\circ}_{298} - H^{\circ}_0$ ), and entropies of the five N-containing ligands—ammonia, methylamine, ethylamine, acetonitrile, and benzonitrile—and their argentinated complexes. Calculated vibrational frequencies and rotational constants employed in the  $E_0$  determinations are listed in Table 1s in Supporting Information. The optimum B3LYP geometries of the ligands and their sodiated complexes are illustrated in Figure 2. Computational data for ammonia were taken from our earlier publication (Shoeib et al.<sup>45</sup>), and those for the nitriles were from Shoeib et

al.<sup>41</sup> They are reproduced here for discussion. Similar to the trend observed for sodiated complexes, the  $\text{Ag}^+ - \text{N}$  bond distance increases in the series benzonitrile < acetonitrile < ethylamine < methylamine = ammonia. For argentinated complexes, the global correlation between bond distance and binding energy is less apparent (vide infra). However, within the amine or the nitrile group, the trend of increasing bond distance with decreasing binding energy is still evident. The differences between sodiated and argentinated complexes reflect differences in metal binding; the covalent character in the  $\text{Ag}^+ - \text{N}$  bond is more prominent than that in the  $\text{Na}^+ - \text{N}$  bond, thus the chemical environment of the nitrogen (i.e., whether it be an amine or nitrile nitrogen) is likely to have a more substantial effect on  $\text{Ag}^+ - \text{N}$  binding than on  $\text{Na}^+ - \text{N}$  binding. As an example of the more prominent covalent character of the  $\text{Ag} - \text{N}$  bond versus that of the  $\text{Na} - \text{N}$  bond, consider the Mülliken charges on  $\text{Ag}^+ - \text{NH}_3$  and  $\text{Na}^+ - \text{NH}_3$ . For the former,

**TABLE 4: Electronic Energies, Zero-Point Vibrational Energies (ZPVE), Thermal Energies, and Entropies of the Ligands and Their Ag<sup>+</sup> Complexes from B3LYP/DZVP Calculations**

species	electronic energy hartrees	ZPVE kcal/mol	$H_{298}^{\circ} - H_{0}^{\circ}$ kcal/mol	entropy cal/(K mol)
ammonia	-56.56404	21.7	2.4	48.2
methylamine	-95.87057	40.3	2.8	57.4
ethylamine	-135.19069	58.3	3.4	64.9
acetonitrile	-132.76885	28.5	2.9	60.3
benzonitrile	-324.51672	62.1	4.5	78.7
Ag <sup>+</sup> -ammonia	-5255.83100	24.1	2.9	64.0
Ag <sup>+</sup> -methylamine	-5295.14003	42.3	3.5	72.4
Ag <sup>+</sup> -ethylamine	-5334.46288	60.0	4.4	80.0
Ag <sup>+</sup> -acetonitrile	-5332.03383	29.1	4.1	77.6
Ag <sup>+</sup> -benzonitrile	-5523.78747	62.8	5.8	95.2
Ag <sup>+</sup>	-5199.19815		1.5	39.9

<sup>a</sup> Sum of translational, vibrational, and rotational energies required to convert between 0 and 298 K.

**TABLE 5: Threshold Binding Energies of Ag<sup>+</sup> to Ligands**

ligand	$E_0$ eV	$E_0$ (PSL) eV	$\Delta S^{\ddagger}$ (PSL) <sup>a</sup> cal/(K mol)
ammonia	1.76 ± 0.13	1.76 ± 0.13	7.41
methylamine	1.80 ± 0.10	1.80 ± 0.10	7.90
ethylamine	1.91 ± 0.06	1.86 ± 0.06	7.68
acetonitrile	1.77 ± 0.09	1.77 ± 0.09	2.39
benzonitrile	2.09 ± 0.12	1.80 ± 0.12	5.35

<sup>a</sup> Entropy of activation at 1000 K.

**TABLE 6: Experimental and Calculated Binding Energies of Ag<sup>+</sup> to Ligands at 0 K<sup>a</sup> (kcal/mol)**

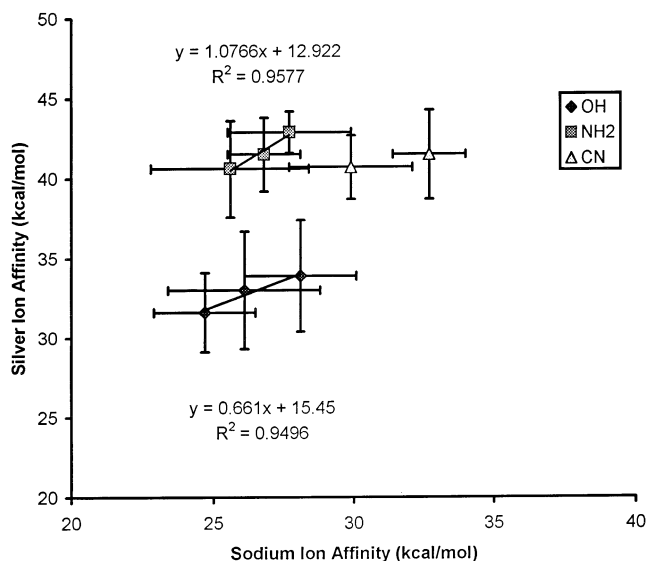
ligand	threshold CID	DFT	$\Delta H_{298}^{\circ} - \Delta H_{0}^{\circ}$ <sup>b</sup>	literature
ammonia	40.6 ± 3.0	38.9 (1.9) <sup>c</sup>	1.0	43.0 <sup>d</sup> , 43.3 <sup>e</sup> , 44.9 <sup>f</sup> , 42.4 <sup>d</sup>
methylamine	41.5 ± 2.3	41.1 (1.6)	0.8	
ethylamine	42.9 ± 1.4	43.2 (1.6)	0.5	
acetonitrile	40.8 ± 2.0	39.3 (2.0)	0.3	43.3 <sup>f</sup>
benzonitrile	41.5 ± 2.8	43.1 (1.8)	0.2	

<sup>a</sup> Literature values not at 0 K have been converted to that temperature.

<sup>b</sup> Difference in enthalpy changes required to convert the binding energy between 0 and 298 K. <sup>c</sup> BSSE correction, which has been incorporated into the DFT binding energy. <sup>d</sup> Reference 46. <sup>e</sup> Reference 43. <sup>f</sup> Reference 44.

Ag, +0.821; N, -1.086; and H, +0.422; for the latter, Na, +0.917; N, -0.756; and H, +0.280. The charge distributions clearly show that the metal–ligand bond in Ag<sup>+</sup>–NH<sub>3</sub> bears a more prominent covalent character than that in Na<sup>+</sup>–NH<sub>3</sub>. This trend is also evident in the other four pairs of metal–ligand complexes.

The  $E_0$  values of the argentinated complexes are shown in Table 5. The raw data for acetonitrile were taken from Shoeb et al.<sup>41</sup> but were reevaluated in this study after the effects of the ion energy distribution and the thermal motion of argon were taken into consideration;<sup>23</sup> this had the effect of increasing the binding energy by 2 kcal/mol (vide infra). The acetonitrile value in Table 5 is the reevaluated  $E_0$  value. Again, benzonitrile is the only ligand whose complex exhibits any significant kinetic shift in its dissociation. The  $E_0$ (PSL) values are converted to Ag<sup>+</sup> binding energies in Table 6. B3LYP/DZVP results and literature values are also given in this Table. The BSSE values are in parentheses. As in the case of sodiated complexes, there is good agreement between experimental and calculated Ag<sup>+</sup> binding energies. The differences between them range from a low of 0.3 kcal/mol for ethylamine to a high of 1.7 kcal/mol for ammonia, which are well within the range of experimental uncertainties of 1.4–3.0 kcal/mol. There is necessarily a compromise between computational efficiency and accuracy in



**Figure 3.** Silver ion affinity versus sodium ion affinity:  $\blacklozenge$ , water, methanol, and ethanol (data from ref 22);  $\blacksquare$ , ammonia, methylamine, and ethylamine;  $\triangle$  acetonitrile and benzonitrile.

our DFT calculations, but the DZVP basis set was specially developed to work with DFT.<sup>50,51</sup> Thus, the good agreement between theory and experiment is reassuring but not surprising. In comparison, literature data<sup>43,44,46</sup> all appear to fall in the vicinity of the +3 kcal/mol edge of acceptability from the experimental data. These published data were based on calculations using effective core potentials with a set of f polarization functions on the Ag atom; the ligands were described by Pople basis sets such as STO-3G,<sup>44</sup> 3-21G(d),<sup>44</sup> 6-31G(d),<sup>46</sup> 6-31+G(d,p),<sup>44</sup> and 6-311++G(d,p).<sup>43</sup> The methods include additivity schemes,<sup>44</sup> MP2,<sup>43</sup> and B3LYP.<sup>46</sup> The employment of effective core potentials is most likely the major contribution in overestimating the binding energies.

**Comparison between Na<sup>+</sup> and Ag<sup>+</sup> Binding Energies.** The silver ion affinities of the five ligands in this study and those of water, methanol, and ethanol measured in our earlier study<sup>23</sup> are plotted against the sodium ion affinities of these eight ligands in Figure 3. It is evident that the data fall into three groups—the alcohols, amines, and nitriles—each with its apparent correlation within the group. The silver ion affinity is larger than the corresponding sodium ion affinity for every ligand, but the magnitude of the difference decreases from the amines to the nitriles and to the alcohols. The preference for Ag<sup>+</sup> to Na<sup>+</sup> exhibited by the N-containing ligands (in comparison to the O-containing ligands) is conventionally rationalized using the hard and soft acid/base principle.<sup>79</sup> Thus, the softer N-containing ligands would prefer the softer Ag<sup>+</sup>, and the harder O-containing ligands, the harder Na<sup>+</sup>. For gas-phase ions, however, this concept has recently been shown to play only a secondary role to electrostatic interaction and is apparent only when the charge of the metal ion is effectively delocalized onto the ligand(s).<sup>80</sup> The nitrogen atom in amines is better able to accommodate the positive charge of Ag<sup>+</sup> than that of Na<sup>+</sup>. It would appear that this difference in preference is further enhanced when electron-donating substituents (alkyl groups) are present; however, the number of data points is too small to draw any definitive conclusions.

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**Supporting Information Available:** Vibrational frequencies and rotational constants of the ligands and the metal complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
- Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life: An Introduction and Guide*; Wiley & Sons: New York, 1994.
- Pettit, L. D.; Gregor, J. E.; Kozlowski, H. Complex Formation between Metal Ions and Peptides. In *Perspectives on Bioinorganic Chemistry*; Hay, R. W., Dilworth, J. R., Nolan, K. B., Eds.; Jai Press: London, 1991; Vol. 1, pp 1–41.
- Petering, H. G. *Pharmacol. Ther., Part A* **1976**, *1*, 127–130.
- Wigley, R. A.; Brooks, R. R. In *Noble Metals and Biological Systems*; Brooks, R. R., Ed.; CRC Press: Boca Raton, FL, 1992; pp 277–297.
- Nomiya, K.; Onoue, K. I.; Kondoh, Y.; Kasuga, N. C.; Nagano, H.; Oda, M.; Sakuma, S. *Polyhedron* **1995**, *14*, 1359–1367.
- Nomiya, K.; Kondoh, Y.; Nagano, H.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1679–1680.
- Narula, S. S.; Mehra, R. K.; Winge, D. R.; Armitage, I. M. *J. Am. Chem. Soc.* **1991**, *113*, 9354–9358.
- Stillman, M. J.; Presta, A.; Gui, Z.; Jiang, D.-T. In *Metal-Based Drugs*; Gielen, M., Ed.; Freund: London, 1994; Vol. 1, pp 375–393.
- Gui, Z.; Green, A. R.; Kasrai, M.; Bancroft, G. M.; Stillman, M. J. *Inorg. Chem.* **1996**, *35*, 6520–6529.
- Hoyau, S.; Norrman, K.; McMahon, T. B.; Ohanessian, G. *J. Am. Chem. Soc.* **1999**, *121*, 8864–8875.
- McMahon, T. B.; Ohanessian, G. *Chem.—Eur. J.* **2000**, *6*, 2931–2941.
- Armentrout, P. B.; Rodgers, M. T. *J. Phys. Chem. A* **2000**, *104*, 2238–2247.
- Rodgers, M. T.; Armentrout, P. B. *Mass Spectrom. Rev.* **2000**, *19*, 215–247.
- Petrie, S. *J. Phys. Chem. A* **2001**, *105*, 9931–9938.
- Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466–1474.
- Castleman, A. W.; Holland, P. M.; Lindsay, D. M.; Peterson, K. I. *J. Am. Chem. Soc.* **1978**, *100*, 6039–6045.
- Guo, B. C.; Conklin, B. J.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6506–6510.
- Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6125–6133.
- Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101–4103.
- Rodgers, M. T.; Armentrout, P. B. *J. Phys. Chem. A* **1999**, *103*, 4955–4963.
- Valina, A. B.; Amunugama, R.; Huang, H.; Rodgers, M. T. *J. Phys. Chem. A* **2001**, *105*, 11057–11068.
- El Aribi, H.; Shoeb, T.; Ling, Y.; Rodriguez, C. F.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. A* **2002**, *106*, 2908–2914.
- Li, H.; Siu, K. W. M.; Guevremont, R.; Le Blanc, J. C. Y. *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 781–792.
- Li, H.; Lee, V. W.-M.; Lau, T.-C.; Guevremont, R.; Siu, K. W. M. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 760–766.
- Lee, V. W.-M.; Li, H.; Lau, T.-C.; Siu, K. W. M. *J. Am. Chem. Soc.* **1998**, *120*, 7302–7309.
- Chu, I. K.; Guo, X.; Lau, T.-C.; Siu, K. W. M. *Anal. Chem.* **1999**, *71*, 2364–2372.
- Rodriguez, C. F.; Shoeb, T.; Chu, I. K.; Siu, K. W. M.; Hopkinson, A. C. *J. Phys. Chem. A* **2000**, *104*, 5335–5342.
- Chu, I. K.; Shoeb, T.; Guo, X.; Rodriguez, C. F.; Lau, T.-C.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 163–175.
- Shoeb, T.; Rodriguez, C. F.; Siu, K. W. M.; Hopkinson, A. C. *Phys. Chem. Chem. Phys.* **2001**, *3*, 853–861.
- Shoeb, T.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. B* **2001**, *105*, 12399–12409.
- Shoeb, T.; Cunje, A.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 408–416.
- Shoeb, T.; Siu, K. W. M.; Hopkinson, A. C. *J. Phys. Chem. A* **2002**, *106*, 6121–6128.
- Chu, I. K.; Cox, D. M.; Guo, X.; Kireeva, I.; McDermott, J. C.; Siu, K. W. M. *Anal. Chem.* **2002**, *74*, 2072–2082.
- Talaty, E. R.; Perera, B. A.; Gallardo, A. L.; Barr, J. M.; Van Stipdonk, M. J. *J. Phys. Chem. A* **2001**, *105*, 8059–8068.
- Barr, J. M.; Van Stipdonk, M. J. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 566–578.
- Cerda, B. A.; Cornett, L.; Wesdemiotis, C. *Int. J. Mass Spectrom.* **1999**, *193*, 205–226.
- Garrison, J. C.; Simons, R. S.; Talley, J. M.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2001**, *20*, 1276–1278.
- Chen, R.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 832–839.
- Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195–4205.
- Shoeb, T.; El Aribi, H.; Siu, K. W. M.; Hopkinson, A. C. *J. Phys. Chem. A* **2001**, *105*, 710–719. Shoeb, T.; El Aribi, H.; Siu, K. W. M.; Hopkinson, A. C. *J. Phys. Chem. A* **2001**, *105*, 1383–1384 (additions and corrections).
- Ho, Y.-P.; Yang, Y.-C.; Klippenstein, S. J.; Dunbar, R. C. *J. Phys. Chem. A* **1997**, *101*, 3338–3347.
- Chattaraj, P. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 1067–1071.
- Ma, N. L. *Chem. Phys. Lett.* **1998**, *297*, 230–238.
- Shoeb, T.; Milburn, R. K.; Koyanagi, G. K.; Lavrov, V. V.; Bohme, D. K.; Siu, K. W. M.; Hopkinson, A. C. *Int. J. Mass Spectrom.* **2000**, *201*, 87–100.
- Boutreau, L.; Leon, E.; Luna, A.; Toulhoat, P.; Tortajada, J. *Chem. Phys. Lett.* **2001**, *338*, 74–82.
- Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571.
- Godbout, N. Ensemble de base pour la théorie de la fonctionnelle de la densité—Structures moléculaires, propriétés mono-électroniques et modèles de zéolites. Ph.D. Dissertation, Université de Montréal, Montréal, Canada, 1996.
- Douglas, D. J. *J. Phys. Chem.* **1982**, *86*, 185–191.
- Douglas, D. J.; French, J. B. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 398–408.
- Covey, T.; Douglas, D. J. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 616–623.
- Goeringer, D. E.; Asano, K. G.; McLuckey, S. A. *Int. J. Mass Spectrom.* **1999**, *182/183*, 275–288.
- Asano, K. G.; Goeringer, D. E.; McLuckey, S. A. *Int. J. Mass Spectrom.* **1999**, *185–187*, 207–219.
- Draho, L.; Heeren, R. M. A.; Collette, C.; De Pauw, E.; Vékey, K. *J. Mass Spectrom.* **1999**, *34*, 1373–1379.
- Schneider, B. B.; Chen, D. D. Y. *Anal. Chem.* **2000**, *72*, 791–799.
- Schneider, B. B.; Douglas, D. J.; Chen, D. D. Y. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 772–779.
- Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 205–211.
- Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1985**, *83*, 166–189.
- Weber, M. E.; Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 1521–1529.
- Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590–8601.
- Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519–3528.
- Shvartsburg, A. A.; Ervin, K. M.; Frederick, J. H. *J. Chem. Phys.* **1996**, *104*, 8458–8469.
- Rodgers, M. T.; Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1997**, *106*, 4499–4508.
- Rodgers, M. T.; Armentrout, P. B. *J. Chem. Phys.* **1998**, *109*, 1787–1800.
- Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, U.K., 1990.
- Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. *J. Phys. Chem.* **1996**, *100*, 12771–12800.
- Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; Wiley & Sons: New York, 1996.
- Klassen, J. S.; Kebarle, P. *J. Am. Chem. Soc.* **1997**, *119*, 6552–6563.
- Klassen, J. S.; Anderson, S. G.; Blades, A. T.; Kebarle, P. *J. Phys. Chem.* **1996**, *100*, 14218–14227.
- Lifshitz, C.; Wu, R. L. C.; Tiernan, T. O.; Terwilliger, D. T. *J. Chem. Phys.* **1978**, *68*, 247–260.
- Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746–2759.

(75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon,

M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(76) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(77) Ketvirtis, A. E.; Bohme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* **1995**, *99*, 16121–16127.

(78) Rodriguez, C. F.; Bohme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* **1996**, *100*, 2942–2949.

(79) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions*, 2nd ed.; Wiley & Sons: New York, 1967.

(80) Shoeib, T.; Gorelsky, S. I.; Lever, A. B. P.; Siu, K. W. M.; Hopkinson, A. C. *Inorg. Chim. Acta* **2001**, *315*, 236–239.