Formation of Abundant [Pb(H$_2$O)]$^{2+}$ by Ligand-Exchange Reaction between [Pb(N$_2$)$_n$]$^{2+}$ (n = 1−3) and H$_2$O

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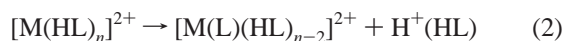*Received: March 7, 2005; In Final Form: April 5, 2005*

Doubly charged lead monohydrate, [Pb(H$_2$O)]$^{2+}$, was predicted to be unstable in the gas phase, but it has recently been observed to form in low yield via ligand change between [Pb(CH$_3$CN)]$^{2+}$ and H$_2$O [Shi, T.; Orlova, G.; Guo, J.; Bohme, D. K.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Chem. Soc.* **2004,** *126,* 7975−7980]. Here we report that *abundant* [Pb(H$_2$O)]$^{2+}$ is formed in the gas phase by ligand-exchange reaction between [Pb(N$_2$)$_n$]$^{2+}$ (n = 1−3) and water after collisional activation. Density functional theory has been used to examine the ligand-exchange reaction profile. A comparison of the potential-energy surfaces between [Pb(N$_2$)]$^{2+}$ and [Pb(CH$_3$CN)]$^{2+}$ reacting with H$_2$O provides strong evidence that the ligand-exchange reaction of [Pb(N$_2$)]$^{2+}$ with H$_2$O to form [Pb(H$_2$O)]$^{2+}$ is more efficient than that of [Pb(CH$_3$CN)]$^{2+}$ with H$_2$O.
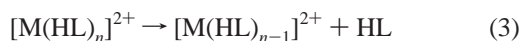
Introduction

Whether doubly charged metal hydrates, [M(H$_2$O)]$^{2+}$, can exist in the gas phase or not has received a lot of attention in the past decade.[1−15] The classical technique of attaching a water molecule to M^{2+} to form [M(H$_2$O)]$^{2+}$ failed except for M = Ba, Sr, and Ca,[16] metals whose second ionization energies (IEs) are lower than the first IE of water at 12.6 eV.[17] For M whose second IEs are higher than the first IE of water, a spontaneous dissociative electron transfer occurs, resulting in M$^{\bullet+}$ and H$_2$O$^{\bullet+}$. It turns out that the route to [M(H$_2$O)]$^{2+}$ is through collision-induced dissociation (CID) of [M(H$_2$O)$_n$]$^{2+}$ ($n \geq 4$), which are abundantly produced via electrospraying an aqueous solution of the M^{2+}.[1,2,11] To date, most [M(H$_2$O)]$^{2+}$ of divalent M, including [Cu(H$_2$O)]$^{2+}$ (Cu has the highest second IE of all divalent metals), have been observed, at least within the tens of microsecond observation window in a tandem mass spectrometry (MS/MS) experiment.[10,11,18] A driving force behind the reactivity of [M(H$_2$O)$_n$]$^{2+}$ and in general [M(HL)$_n$]$^{2+}$, where HL is a generic ligand, is its high charge density, especially when n is small. A classical view is that withdrawal of electron density from the ligand to the formally doubly charged metal ion provides some stabilization and causes partial delocalization of the 2+ charge onto the ligands. This delocalization predisposes the complex to dissociation as a result of Coulombic repulsion. Dissociation can take place concomitantly with electron transfer:

$$[M(HL)_n]^{2+} \rightarrow [M(HL)_{n-1}]^{\bullet+} + HL^{\bullet+} \qquad (1)$$
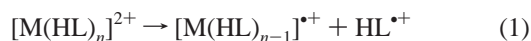
or with proton transfer:

$$[M(HL)_n]^{2+} \rightarrow [M(L)(HL)_{n-2}]^{2+} + H^+(HL) \qquad (2)$$

These two channels compete with ligand elimination:

$$[M(HL)_n]^{2+} \rightarrow [M(HL)_{n-1}]^{2+} + HL \qquad (3)$$

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In general, dissociative electron and/or proton transfer are/is more prevalent than ligand elimination in the CID of [M(HL)$_n$]$^{2+}$ where n is small.

For HL = H$_2$O, high-level ab initio calculations performed on [M(H$_2$O)]$^{2+}$ for a number of alkaline earth and transition metal ions have all predicted the presence of sizable activation barriers in the dissociative electron-transfer reactions into M$^{\bullet+}$ and H$_2$O$^{\bullet+}$, and that the [M(H$_2$O)]$^{2+}$ is either stable or metastable.[7−9] Beyer et al.[7] showed using density functional theory (DFT) that alkaline earth metal dihydrates [M(H$_2$O)$_2$]$^{2+}$ dissociate preferentially via proton transfer to give MOH$^+$ and H$_3$O$^+$. The [M(H$_2$O)$_2$]$^{2+}$ complexes are nonetheless stable as the activation energies for dissociative proton transfer are larger than 33 kcal/mol.[7]

Despite electrospray's success in producing [M(H$_2$O)]$^{2+}$ of most divalent metals, attempts to produce [Pb(H$_2$O)$_n$]$^{2+}$ ions by electrospraying lead(II) salt solutions were unsuccessful. By contrast, the complexes [Pb(CH$_3$CN)$_n$]$^{2+}$,[15] [Pb(D-glucose)$_n$]$^{2+}$,[19] and [Pb(DMSO)$_n$]$^{2+}$ [20] have been produced by electrospray. Stace et al.[21] using the "pick-up" technique, also failed to detect any [Pb(H$_2$O)$_n$]$^{2+}$ ions in the gas phase, but did observe doubly charged ions [Pb(ROH)$_n$]$^{2+}$, where ROH was propan-1-ol or butan-1-ol. These experiments, complemented by DFT calculations, allowed them to deduce that the stability of [Pb(ROH)$_4$]$^{2+}$ could be explained by the hard−soft acid−base principle and led them to the conclusion that complexes of smaller alcohols and water with Pb^{2+} are too unstable to exist. However, very recently, we provided proof that doubly charged lead monohydrate does exist and can be synthesized, albeit in very low yield, by the ligand-exchange reaction between [Pb(CH$_3$CN)]$^{2+}$ and water in the collision cell of a tandem mass spectrometer.[15] DFT calculations show strong evidence that [Pb(H$_2$O)]$^{2+}$ is stable, while [Pb(H$_2$O)$_2$]$^{2+}$ and [Pb(H$_2$O)$_3$]$^{2+}$ are metastable against dissociative proton transfer.

Here we report that abundant [Pb(H$_2$O)]$^{2+}$ can be produced via the ligand-exchange reaction between [Pb(N$_2$)$_n$]$^{2+}$ (n = 1−3) and water. By comparison with the reaction between [Pb(CH$_3$CN)]$^{2+}$ and water, factors that lead to efficient production of [Pb(H$_2$O)]$^{2+}$ are presented and discussed.

TABLE 1: Relative Abundances of Product Ions from Collisional Activation^a of [^{208}Pb(CH$_3$CN)]$^{2+}$ and [^{208}Pb(N$_2$)$_n$]$^{2+}$ with Wet Nitrogen (6 mTorr) under Multiple-Collision Conditions

complex	% of total ion signal				
	Pb$^{•+}$	PbOH$^+$	Pb^{2+}	[Pb(H$_2$O)]$^{2+}$	precursor ion
[Pb(CH$_3$CN)]$^{2+}$	51.0	3.7	3.7	0.08	32.9
[Pb(N$_2$)]$^{2+}$	25.4	18.6	18.1	14.7	23.2
[Pb(N$_2$)$_2$]$^{2+}$	20.5	29.1	7.3	21.8	3.1
[Pb(N$_2$)$_3$]$^{2+}$	13.6	37.2	3.4	22.8	2.4

^{a} [Pb(CH$_3$CN)]$^{2+}$, 40 eV; [Pb(N$_2$)$_n$]$^{2+}$, 10 eV.

Figure 1. Collisional activation of (a) [^{206}Pb(N$_2$)]$^{2+}$, (b) [^{208}Pb(N$_2$)]$^{2+}$, (c) [^{206}Pb(N$_2$)$_3$]$^{2+}$, and (d) [^{208}Pb(N$_2$)$_3$]$^{2+}$, by and reaction with wet nitrogen. Laboratory collision energy, 10 eV; collision gas pressure, 6 mTorr. The performance characteristics of Q1 were such that ions within +0.5 Th from the mass-selected ion were more efficiently transmitted than those within −0.5 Th, resulting in observation of ^{207}Pb in the spectra of (a) and (c), but not in those of (b) and (d).

Experimental Section

Experiments were performed on a prototype mass spectrometer that is similar in design to the Applied Biosystems/MDS SCIEX API 3000 triple-quadrupole mass spectrometer. This prototype instrument has a lower mass-to-charge limit of 30 Th (similar to the API 3000 mass spectrometer). The sample was 200 μM lead(II) nitrate in acetonitrile and was introduced into the ion source by electrospraying at a flow rate of 3 μL/min. The lens voltages were optimized to produce [Pb(N$_2$)$_n$]$^{2+}$ ($n = 1-3$). All chemicals and solvents were available from Sigma/Aldrich (St. Louis, MO). MS/MS experiments were performed by mass-selecting the precursor ions using the first quadrupole mass analyzer (Q1), colliding them with 1−12 mTorr of wet nitrogen in the second quadrupole (q2), and mass-analyzing with the third quadrupole (Q3). The nitrogen was boiled off from liquid nitrogen, which contained water as a contaminant. Water is a ubiquitous contaminant of liquid nitrogen; its concentration in the nitrogen used is unknown (see below).

Computational Section

Geometry optimizations and energy calculations were performed with Gaussian 98.[22] The B3LYP exchange-correlation functional[23−25] with the sdd relativistic effective core potential (ECP)[26] was used for lead and the 6-31++G** doubly split-valence basis set[27−30] was used for the other atoms. All stationary points were characterized by harmonic vibrational frequency calculations. Connections between transition states and corresponding minima were verified using the intrinsic reaction coordinate (IRC) method.[31,32] Relative enthalpies at 0 K and relative free energies at 298 K are reported. Cartesian coordinates and electronic energies for key structures are available as Supporting Information.

Results and Discussion

Under a declustering potential of 80−120 eV, electrospraying an acetonitrile solution of lead(II) nitrate produced Pb^{2+} in high abundance. A small fraction of the Pb^{2+}, after supersonic jet expansion, associated with N$_2$, the curtain gas, a minute fraction
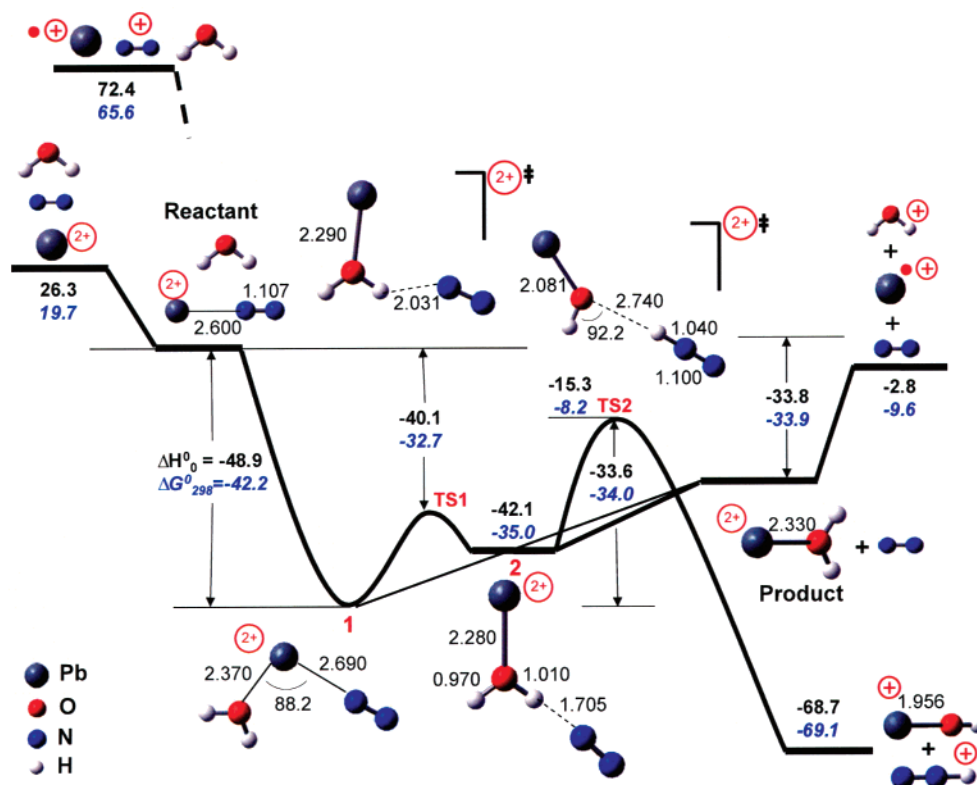
Figure 2. Reaction profiles of [Pb(N$_2$)]$^{2+}$ and water at B3LYP/sdd/6-31++G**. The upper values are relative enthalpies at 0 K ($\Delta H°_0$); the lower, italicized values are relative free energies at 298 K ($\Delta G°_{298}$). All energies are in kcal/mol.

of which was also sampled along with Pb^{2+} and other ions. Up to three nitrogen molecules could be attached, resulting in [Pb-(N$_2$)$_n$]$^{2+}$ ($n = 1-3$). Mass-selecting [Pb(N$_2$)$_n$]$^{2+}$ ($n = 1-3$) by Q1, colliding with wet nitrogen in q2, and mass-analyzing by Q3 resulted in a number of product ions, including Pb$^{•+}$, PbOH$^+$, [Pb(N$_2$)]$^{2+}$, Pb^{2+}, and [Pb(H$_2$O)]$^{2+}$. Their relative abundances are summarized in Table 1; mass spectra for [^{206}Pb(N$_2$)]$^{2+}$, [^{208}Pb(N$_2$)]$^{2+}$, [^{206}Pb(N$_2$)$_3$]$^{2+}$, and [^{208}Pb(N$_2$)$_3$]$^{2+}$ are shown in Figure 1. Table 1 also summarizes the results of colliding [Pb-(CH$_3$CN)]$^{2+}$ with wet nitrogen; it is readily apparent that more [Pb(H$_2$O)]$^{2+}$ was produced from [Pb(N$_2$)$_n$]$^{2+}$ ($n = 1-3$) than from [Pb(CH$_3$CN)]$^{2+}$. The relative abundance of [Pb(H$_2$O)]$^{2+}$ increased from the latter to the former by a factor of ca. 180 for $n = 1$ and ca. 280 for $n = 3$. In an earlier paper, we reported the synthesis of [Pb(H$_2$O)]$^{2+}$ via colliding [Pb(CH$_3$CN)]$^{2+}$ with room air of relative humidity of 50−58%.[15] Although the moisture content of the wet nitrogen used in the current study is unknown, it is unlikely that it is as high as that of room air. This conjecture is in accordance with the measured relative abundance of [Pb(H$_2$O)]$^{2+}$ at 0.08% (Table 1), which is lower than that measured previously at 0.4%.[15] By contrast, with [Pb-(N$_2$)$_n$]$^{2+}$ as reagent, [Pb(H$_2$O)]$^{2+}$ is a major product ion with relative abundance ranging from 14.7 to 22.8% from $n = 1$ to $n = 3$. As in our earlier proposal,[15] we are hypothesizing here that the abundant [Pb(H$_2$O)]$^{2+}$ observed in this study was a result of ligand-exchange reaction between the Pb^{2+} complex, herein [Pb(N$_2$)$_n$]$^{2+}$, and H$_2$O:

$$[Pb(N_2)_n]^{2+} + H_2O \rightleftharpoons \{[Pb(N_2)_n(H_2O)]^{2+}\}^* \rightarrow$$
$$[Pb(H_2O)]^{2+} + nN_2 \quad (4)$$
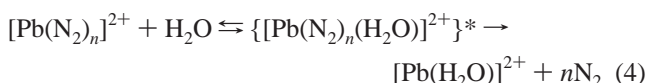
where the asterisk (*) denotes vibronical excitation. The higher yield of [Pb(H$_2$O)]$^{2+}$ from [Pb(N$_2$)$_3$]$^{2+}$ than from [Pb(N$_2$)]$^{2+}$ may be attributed to, first, a longer lifetime of the {[Pb(N$_2$)$_3$-

(H$_2$O)]$^{2+}$}* complex than that of the {[Pb(N$_2$)(H$_2$O)]$^{2+}$}* complex because of the increased degrees of freedom by having two additional nitrogen molecules and, second, a more efficient deactivation of [Pb(H$_2$O)]$^{2+}$ because of the presence of two additional nitrogen molecules into which the excess energy may be distributed after dissociation.

Prior to examining the reaction channels of [Pb(N$_2$)$_n$]$^{2+}$ with water, it is instructive to examine the properties of the nitrogen molecule. For comparison, we will also examine the properties of acetonitrile. N$_2$ has a triple bond, which is much stronger (226.2 ± 0.1 kcal/mol) than the C−C bond of acetonitrile (145.9 ± 0.5 kcal/mol),[17] suggesting that, unlike acetonitrile, ligand fragmentation will not occur with N$_2$ in [Pb(N$_2$)$_n$]$^{2+}$. The bond enthalpy, $\Delta H°_0$, for the M−ligand bond in [Pb(N$_2$)]$^{2+}$ is 26.3 kcal/mol (see below), 65.6 kcal/mol lower than that in [Pb-(CH$_3$CN)]$^{2+}$ at 91.9 kcal/mol.[15] Thus the loss of the nitrogen molecule is much easier than that of acetonitrile. That is, the stabilities of [Pb(N$_2$)$_n$]$^{2+}$ are much lower than those of [Pb-(CH$_3$CN)$_n$]$^{2+}$. Indeed, in MS scans, we found that the abundances of [Pb(N$_2$)$_n$]$^{2+}$ are lower and more sensitive to orifice voltages than those of [Pb(CH$_3$CN)$_n$]$^{2+}$. In addition, the IE of N$_2$ (15.6 eV) is slightly higher than the second IE of Pb (15.0 eV), while the IE of CH$_3$CN (12.2 eV) is lower.[17] This means that electron transfer from the nitrogen molecule to doubly charged lead is unlikely. The wet nitrogen contains traces of water and oxygen. The IEs of H$_2$O (12.6 eV) and O$_2$ (12.1 eV) are lower than the second IE of lead.[17] Thus electron transfer from water and oxygen to Pb^{2+} in the transient complexes formed after collision is exothermic and will be efficient, unless the barrier against electron transfer is large. Indeed, O$_2$$^{•+}$ was reported in the earlier, [Pb(CH$_3$CN)]$^{2+}$ work.[15]

The following reaction channels are apparent in the collision of [Pb(N$_2$)]$^{2+}$ with wet nitrogen: (1) ligand elimination, [Pb-(N$_2$)]$^{2+}$ + M → Pb^{2+} + N$_2$ + M (where M is a collision partner,

N_2, O_2, or H_2O); (2) complexation followed by dissociative electron transfer, $Pb^{2+} + O_2$ (or H_2O) → $\{[Pb(O_2$ or $H_2O)]^{2+}\}^*$ → $Pb^{\bullet+} + O_2^{\bullet+}$ (or $H_2O^{\bullet+}$); (3) complexation followed by dissociative proton transfer, $[Pb(N_2)]^{2+} + H_2O$ → $\{[Pb(N_2)-(H_2O)]^{2+}\}^*$ → $PbOH^+ + N_2H^+$; (4) ligand exchange, $[Pb(N_2)]^{2+} + H_2O$ → $\{[Pb(N_2)(H_2O)]^{2+}\}^*$ → $[Pb(H_2O)]^{2+} + N_2$. All ions >30 Th with the exception of $O_2^{\bullet+}$ have been detected (Figure 1); the absence of $O_2^{\bullet+}$ (32 Th) is likely due to scattering and poor confinement within q2.

The reaction profile between $[Pb(N_2)]^{2+}$ and H_2O is shown in Figure 2, where the upper values are ΔH°_0 and the lower, italicized values are ΔG°_{298}. As we have shown experimentally that $[Pb(H_2O)]^{2+}$ exists in the gas phase, our focus here is on the mechanism of the ligand-exchange reaction between $[Pb-(N_2)]^{2+}$ and H_2O. Reaction of $[Pb(N_2)]^{2+}$ and H_2O leads first to the formation of vibronically excited $[Pb(N_2)(H_2O)]^{2+}$, structure **1**, which then dissociates either directly into $[Pb-(H_2O)]^{2+}$ and N_2, or indirectly after promoting the ligated nitrogen from the first to the second solvation shell via the transition state **TS1** to form $[Pb(H_2O)]^{2+}(N_2)$, structure **2**, which then dissociates to form $[Pb(H_2O)]^{2+}$ and N_2 (channel 4). Both dissociations from the vibronically excited structure **1** are expected to be barrierless. Alternatively, **2** can also dissociate via **TS2**, through which a proton is transferred from the ligated water to the departing nitrogen molecule, to give $PbOH^+$ and N_2H^+ (channel 3). There is competition between nitrogen elimination and dissociative proton transfer; this largely determines the formation efficiency of $[Pb(H_2O)]^{2+}$. **TS2** at −15.3 kcal/mol is 18.5 kcal/mol higher in enthalpy than the separated products of $[Pb(H_2O)]^{2+}$ and N_2. Thus formation of $[Pb(H_2O)]^{2+}$ is favored over that of $PbOH^+$. By comparison, for $[Pb(CH_3-CN)(H_2O)]^{2+}$ the formation of $PbOH^+$ is favored over that of $[Pb(H_2O)]^{2+}$ by 48.8 kcal/mol, which is the major factor for low $[Pb(H_2O)]^{2+}$ abundance in the earlier work.[15] It is noteworthy that the barriers for proton transfer are inversely related to the proton affinities of the ligands: the proton affinity of acetonitrile (186.2 kcal/mol) is much higher than that of nitrogen (118.0 kcal/mol).[33] In addition, the dissociative proton-transfer barrier (in terms of ΔH°_0) in $[Pb(CH_3CN)(H_2O)]^{2+}$, at 22.1 kcal/mol,[15] is 11.5 kcal/mol lower than that of $[Pb(N_2)(H_2O)]^{2+}$, at 33.6 kcal/mol. As formation of $[Pb(H_2O)]^{2+}$ involves loss of the ligand originally attached to Pb^{2+}, the binding enthalpies of Pb^{2+} to the ligands are also an important factor. For the ligands N_2, H_2O, and CH_3CN, the calculated binding enthalpies with Pb^{2+} are, respectively, 26.3, 60.4,[15] and 91.9 kcal /mol.[15] Within the context of relative binding enthalpy, collisionally activated $[Pb(N_2)(H_2O)]^{2+}$ would be expected to lose nitrogen, while $[Pb(CH_3CN)(H_2O)]^{2+}$ lose water. Thus all factors discussed above are consistent with the experimental observation: namely, that ligand exchange between $[Pb(CH_3CN)]^{2+}$ and H_2O produces a low abundance of $[Pb(H_2O)]^{2+}$; by contrast, ligand exchange between $[Pb(N_2)]^{2+}$ and H_2O produces $[Pb(H_2O)]^{2+}$ abundantly.

Conclusions

Abundant $[Pb(H_2O)]^{2+}$ is produced in the ligand-exchange reaction of $[Pb(N_2)_n]^{2+}$ with water. Compared to our previous observation, where a low abundance of $[Pb(H_2O)]^{2+}$ was observed in the reaction of $[Pb(CH_3CN)]^{2+}$ with water, the efficiency of ligand exchange in this study is greatly enhanced by having a weakly bound N_2 as the departing ligand. Two properties of the ligand, the proton affinity and the binding enthalpy, contribute toward the formation efficiency of $[Pb-(H_2O)]^{2+}$.

References and Notes

(1) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 251−267.

(2) Cheng, Z. L.; Siu, K. W. M.; Guevremont, R.; Berman, S. S. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 281−288.

(3) Kohler, M.; Leary, J. A. *Int. J. Mass Spectrom. Ion Processes* **1997**, *162*, 17−34.

(4) Stace, A. J.; Walker, N. R.; Firth, S. *J. Am. Chem. Soc.* **1997**, *119*, 10239−10240.

(5) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1998**, *120*, 5842−5843.

(6) Stone, J. A.; Vukomanovic, D. *Int. J. Mass Spectrom. Ion Processes* **1999**, *185−187*, 227−229.

(7) Beyer, M.; Williams, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565−1573.

(8) El-Nahas, A. M. *Chem. Phys. Lett.* **2000**, *329*, 176−178.

(9) El-Nahas, A. M. *Chem. Phys. Lett.* **2001**, *345*, 325−330.

(10) Stone, J. A.; Vukomanovic, D. *Chem. Phys. Lett.* **2001**, *346*, 419−422.

(11) Shvartsburg, A. A.; Siu, K. W. M. *J. Am. Chem. Soc.* **2001**, *123*, 10071−10075.

(12) Shvartsburg, A. A.; Wilkes, J. G.; Lay, J. O.; Siu, K. W. M. *Chem. Phys. Lett.* **2001**, *350*, 216−224.

(13) Shvartsburg, A. A. *J. Am. Chem. Soc.* **2002**, *124*, 12343−12351.

(14) Cox, H.; Akibo-Betts, G.; Wright, R. R.; Walker, N. R.; Curtis, S.; Duncombe, B.; Stace, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 233−242.

(15) Shi, T.; Orlova, G.; Guo, J.; Bohme, D. K.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Chem. Soc.* **2004**, *126*, 7975−7980.

(16) Spears, K. G.; Fehsenfeld, F. C. *J. Chem. Phys.* **1972**, *56*, 5698−5705.

(17) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Roca Baton, FL.

(18) Schröder, D.; Schwarz, H.; Wu, J.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001**, *343*, 258−264.

(19) Salpin, J.-Y.; Tortajada, J. *J. Phys. Chem. A* **2003**, *107*, 2943−2953.

(20) Shvartsburg, A. A.; Wilkes, J. G. *J. Phys. Chem. A* **2002**, *106*, 4543−4551.

(21) Akibo-Betts, G.; Barran, P. E.; Puskar, L.; Duncombe, B.; Cox, H.; Stace, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 9257−9264.

(22) 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.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; 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.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Rev. A. 11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(23) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098−3100.

(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785−789.

(26) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173−194.

(27) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

(28) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217−219.

(29) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609−5612.

(30) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.

(31) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154−2161.

(32) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1990**, *94*, 5523−5527.

(33) Proton affinities are from http://webbook.nist.gov/Chemistry/.