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Gas phase studies of Zn_2^+, Ag_3^+, and Ag_5^+

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Laser desorption from ZnO and AgO produces small bare metal cluster ions. Laser desorption from a ZnO/AgO mixture produces an enhancement of the silver cluster ion signal with complete suppression of the zinc signal. The chemistry of Zn_2^+ indicates $IP(Zn_2) = 9.0 \pm 0.2$ eV and $D^0(Zn^+\text{–}Zn) = 0.56 \pm 0.2$ eV. The reactivity of Zn_2^+ with alkenes and alcohols is characterized by displacement of a zinc atom and formation of $Zn^+\text{–}B$ (B = alcohol, alkene). The silver cluster ions are produced with excess kinetic energy; however, collisional cooling is achieved by trapping the cluster ions in a static pressure of argon. Charge transfer reactions indicate $IP(Ag_n) < 7.0$ eV ($n = 3,5$). Ag_3^+ and Ag_5^+ are unreactive with small alkanes, alkenes, and alcohols, but $Ag_nL_2^+$ ($n = 3,5$; L = sec-butylamine) reacts with sec-butylamine via deamination and dehydrogenation indicating $D^0(Ag_nL_2^+\text{–butadiene}) > 1.73$ eV.

INTRODUCTION

The last few years have seen cluster research develop into one of the most intensely studied areas of chemistry and physics.[1] Much of the interest has been due to the possibility of bridging the gap between gas phase and condensed phase chemistry through the study of clusters.[2] In addition, clusters are of importance because of their role in astrophysics, heterogeneous catalysis, and their possible use in the future development of microelectronics.

Clusters have been studied using a variety of techniques, including supersonic expansion,[3] matrix isolation,[4] ion trapping,[5] and ion beam methods.[6] The ion trapping capability of Fourier transform mass spectrometry (FTMS) allows for control of the size and composition of cluster ions. In addition, collision-induced dissociation (CID), photodissociation, multistep reaction sequences, and control of ion kinetic energy are possible using FTMS.[7]

Smalley and co-workers have recently interfaced a supersonic expansion source with an FTMS.[8] This technique was used to study the dissociative chemisorption of H_2 onto Nb_n^+ ($n = 7$–9).[9] Moini and Eyler[10] and Weil and Wilkins[11] have produced small gold cluster ions by laser desorption from gold and gold oxide, respectively.

In this paper we report on the formation of small zinc and silver cluster ions by laser desorption from their respective oxides. The gas phase thermochemistry and reactivity of Zn_2^+, Ag_3^+, and Ag_5^+ are described, along with a novel reaction observed for $Ag_nL_2^+$ ($n = 3,5$; L = sec-butylamine) with sec-butylamine.

EXPERIMENTAL

Experiments were performed on a Nicolet FTMS-2000 dual cell Fourier transform mass spectrometer[12] with the magnetic field maintained at 3.0 T (see Fig. 1).

Cluster ions were generated by laser desorption from metal oxide pellets using a Quanta Ray Nd:YAG laser (1064 nm) operated in the range of 2–20 mJ/pulse. Metal oxide pellets were introduced to the vacuum chamber on a solids probe.

Swept double resonance ejection techniques were used to isolate cluster ions for subsequent reactions.[13] Argon was present in the cell at a total static pressure of $\sim 2 \times 10^{-6}$ Torr, as measured on a Bayard–Alpert ionization gauge. The Ar was used for CID experiments,[14] as well as for cooling of kinetically excited cluster ions through thermalizing collisions prior to reaction.[15] However, a small population of nonthermal ions may still be present after the collisional cooling period.

Reagent chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Reagents were introduced into the instrument at a static background pressure of $\sim 6 \times 10^{-7}$ Torr. Silver(II) oxide and zinc oxide were obtained in high purity from Aldrich, and pellets of these oxides were prepared using a Parr hand-held pellet press.

RESULTS AND DISCUSSION

Zn_2^+

Direct laser desorption from a ZnO pellet produces Zn^+, Zn_2^+, and small amounts of Zn_2O^+ (< 5%). The ratio

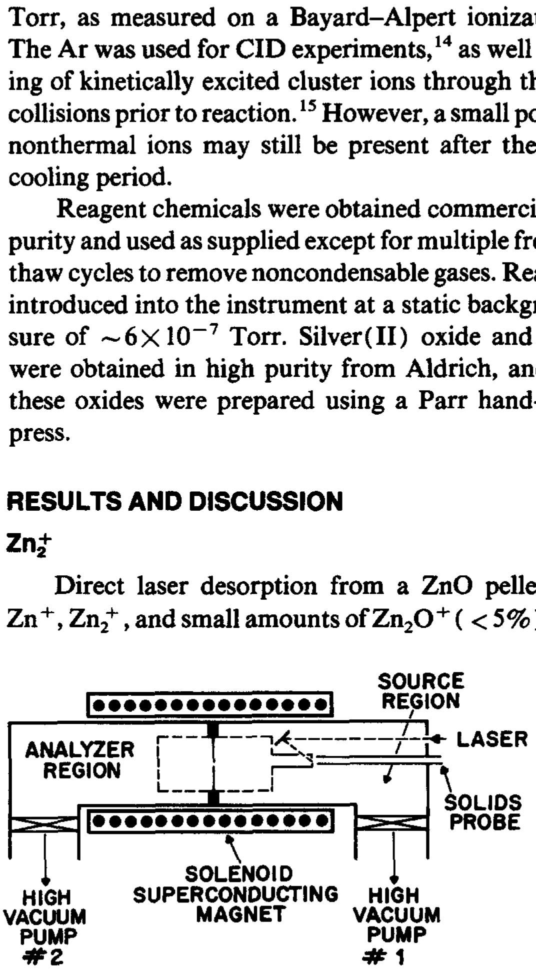

FIG. 1. Differentially pumped dual cell configuration for the Nicolet FTMS-2000 Fourier transform mass spectrometer.

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of Zn^+ to Zn_2^+ is dependent on laser power, with enhancement of clustering occurring at lower powers.

After isolation of Zn_2^+ by swept double resonance ejection methods and cooling of this species through multiple collisions with Ar, the ionization potential of the dimer was bracketed by charge transfer reactions with various neutral reagent gases. One complication in this procedure was interference from displacement reactions which were observed for all of the reagents used. In addition, there is no Zn_2 reagent available which could be admitted into the cell for reionization by the ionized charge transfer reagent. Therefore, the charge transfer reactions are "one sided" and reactions which are slightly endothermic (~ 0.1 eV) may still be observed due to the excess of charge transfer reagent. We have expanded our error limits for the ionization potential to account for these problems. Rapid charge transfer occurs in reactions of Zn_2^+ with cyclohexene, reaction (1), while no charge transfer is observed with 1,3-butadiene, indicating $8.95\ \text{eV} = \text{IP}(c\text{-}C_6H_{10}) < \text{IP}(Zn_2) < \text{IP}(1,3\text{-butadiene}) = 9.07\ \text{eV}$,[16] from which we assign $\text{IP}(Zn_2) = 9.0 \pm 0.2$ eV. A summary of the charge transfer reactions is shown in Table I.

$$Zn_2^+ + c\text{-}C_6H_{10} \rightarrow Zn_2 + c\text{-}C_6H_{10}^+. \qquad (1)$$

Recently, there has been some controversy concerning the value of $D^0(\text{Zn–Zn})$. A number of theoretical reports have suggested that Zn_2 is unbound in the ground state[17]; however, a recent matrix isolation study by Schroeder *et al.* provided evidence indicating a bound ground state,[18] and a value of $D^0(\text{Zn–Zn}) = 0.168$ eV has been reported.[19] Using this value in Eq. (2) yields $D^0(\text{Zn}^+\text{–Zn}) = 0.56 \pm 0.2$ eV.

$$D^0(\text{Zn}^+\text{–Zn}) = D^0(\text{Zn–Zn}) + \text{IP(Zn)} - \text{IP}(Zn_2). \qquad (2)$$

Assuming the bonding in Zn_2^+ is due solely to an ion–induced dipole interaction, an internuclear separation of the dimer can be estimated using

$$V(R) = -e^2\alpha/2R^4, \qquad (3)$$

where α is the polarizability of zinc (7.08 Å^3),[20] e is the unit charge of an electron, R is the internuclear separation in Å, and $V(R) = 0.56$ eV is the value determined above. This yields a value of ~ 3 Å for the internuclear distance which is substantially larger than a value of 2.25 Å obtained by summing the atomic radius of zinc (1.37 Å) and the ionic crystal radius of Zn^+ (0.88 Å). A more reasonable view of the bonding in Zn_2^+ may be a covalent $(4s\sigma_g)^2(4s\sigma_u)$ bond with the completely filled d orbitals of $\text{Zn}(3d^{10}4s^2)$ and $\text{Zn}^+(3d^{10}4s^1)$ remaining primarily atomic in character. This would imply a bond order of one-half with the positive charge shared equally between the Zn atoms. Similar bonding schemes have been proposed for Mn_2^+[21] and Cu_2^-.[22]

The reactivity of Zn_2^+ with alcohols and alkenes is characteristic of a weakly bound cluster. Rapid displacement of a zinc atom to form ZnB^+ ($\text{B} = C_1$–C_3 alcohols, C_2–C_7 alkenes) is the only reaction pathway observed. Similar behavior has been observed by Ridge and co-workers in the chemistry of the weakly bound species Mn_2^+ with various bases.[23]

TABLE I. Results of charge transfer studies with Zn_2^+.[a]

Reagent	IP (reagent) (eV)	Transfer observed	Ligand displacement observed
p-Xylene	8.44	yes	yes
Toluene	8.82	yes	yes
Cyclohexene	8.95	yes	yes
1,3-Butadiene	9.07	no	yes
Benzene	9.25	no	yes
1-Hexene	9.45	no	yes

[a] The observation of charge transfer implies $\text{IP}(Zn_2) > \text{IP(reagent)}$. This assumes the reaction is controlled by thermodynamic, as opposed to kinetic, factors. This assumption has been shown to be valid for many ion–molecule systems in the gas phase (see Ref. 34).

Ag_n^+

Laser desorption from a AgO pellet produces Ag^+, Ag_3^+, and Ag_3O^+. Once again, enhancement of clustering is observed with reduction of laser power. Surprisingly, laser desorption from a pellet containing a mixture of AgO and ZnO produces a further enhancement of the silver clustering, while any Zn^+, Zn_2^+, or mixed Ag/Zn clusters are absent. Utilizing these mixed pellets, silver cluster ions in the range Ag_n^+ ($n = 1$–9) have been observed (see Fig. 2).

This interesting effect may be attributed to the fact that Zn is inert in the gas phase due to its $3d^{10}4s^2$ electronic configuration and Zn^+ only reacts via rapid charge transfer due to its $3d^{10}4s^1$ configuration.[24] Thus, Zn and Zn^+ may act as third bodies, stabilizing silver cluster ions and neutral clusters through collisions in the laser desorbed plasma and promoting the formation of larger silver cluster ions. Alternatively, the ZnO may simply enhance clustering through matrix effects which serve to reduce the laser power at the pellet surface.

The increased ion abundance of odd-numbered cluster ions has been previously observed in studies of silver clusters produced by sputtering from metal surfaces and has been attributed to the higher stability of odd-numbered cluster ions relative to even-numbered cluster ions.[25]

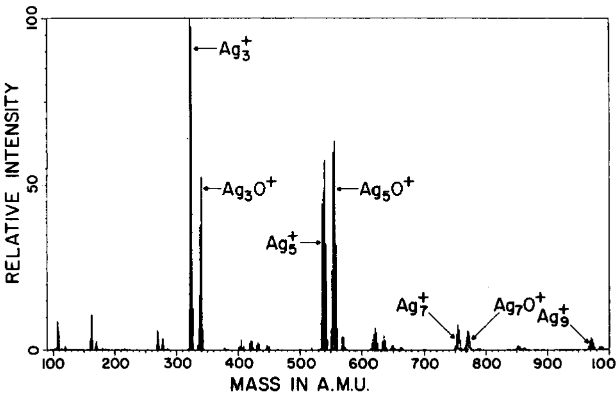


FIG. 2. Mass spectrum of Ag_n^+ ($n = 1$–9) generated by direct laser desorption from a mixed AgO/ZnO pellet. Spectrum shown is an average of five scans.

Collision-induced dissociation of Ag_5^+ produces only Ag_3^+, [reaction (4)] (see Fig. 3), over the entire energy range studied (up to 100 eV lab energy):

$$\mathrm{Ag}_5^+ \xrightarrow{\mathrm{Ar}} \mathrm{Ag}_3^+ + \mathrm{Ag}_2 \text{(up to 100 eV lab energy)}. \qquad (4)$$

Recent photodissociation studies of Ag_5^+ demonstrated that the major fragmentation product was Ag_3^+ with a small amount of Ag_4^+ also observed.[26] Collisional activation of Ag_3^+ produced no observable fragmentation with collision energies up to 100 eV (lab). These results indicate a very small cross section for CID and are consistent with a stable triangular structure for Ag_3^+, which has recently been proposed based on theoretical studies[27] and electron spin resonance experiments.[28]

Atomic and cluster species produced by direct laser desorption or particle bombardment have previously been shown to contain a population of kinetically and internally excited species.[29–31] Ag_3^+ and Ag_5^+ formed by laser desorption undergo rapid charge exchange with ferrocene [reaction (5)]. However, when Ar buffer gas is introduced into the cell, charge transfer is no longer observed:

$$\mathrm{Ag}_n^+ + \mathrm{Fe(C_5H_5)_2} \to \mathrm{Ag}_n + \mathrm{Fe(C_5H_5)_2^+}, \qquad (5)$$
$$(n = 3,5).$$

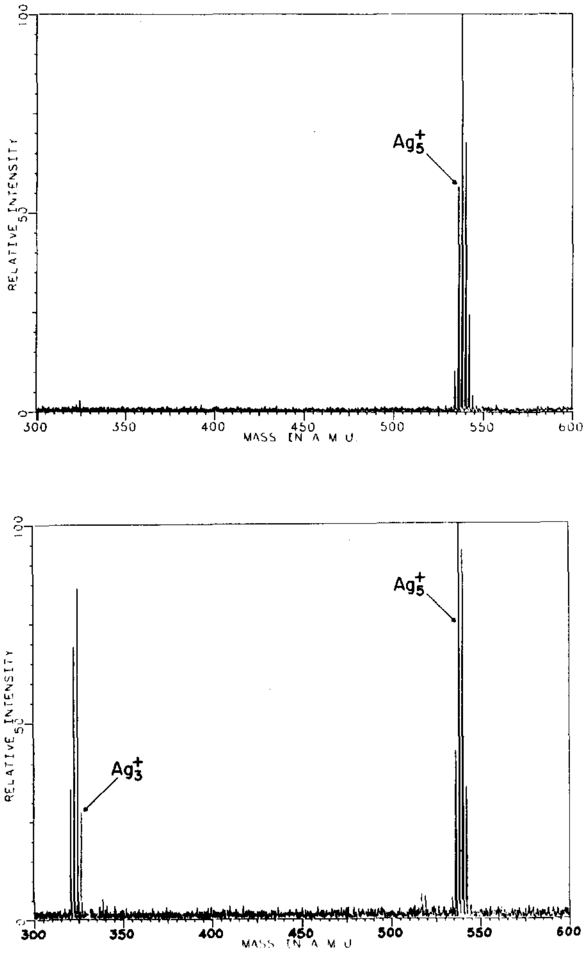


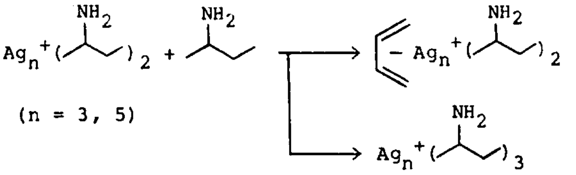
FIG. 3. (a) Isolation of Ag_5^+ after laser desorption from a mixed AgO/ZnO pellet. (b) Collision spectrum of Ag_5^+ at ~50 eV laboratory collision energy. Ag_3^+ is the only product at all collision energies studied (0–100 eV). Deviations of isotopic ratios from those predicted using natural isotopic abundances are due to instrumental tuning effects.

Under these conditions the cluster ions undergo ~20 collisions prior to reaction with ferrocene.[32] Silver cluster ions which have been thermalized can be subsequently kinetically excited by the application of a radio-frequency pulse resonant with the cyclotron frequency of the ions.[33] After kinetic excitation of the cluster ions, charge transfer is once again observed. Thus, it is evident that some fraction of the silver cluster ion population produced by direct laser desorption is kinetically excited. These results impose a rigorous upper limit on the ionization potentials of these clusters:

$$\mathrm{IP(Ag_3), IP(Ag_5)} < \mathrm{IP[Fe(C_5H_5)_2]} = 7.0\ \mathrm{eV}.$$

This upper limit for $\mathrm{IP(Ag_3)}$ is in agreement with a recent value of 6.15 eV obtained with a local spin density pseudopotential calculation.[27]

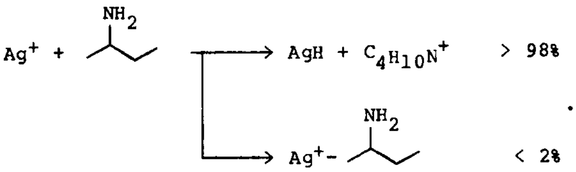
Condensation is the only pathway observed for the reactions of Ag_3^+ and Ag_5^+ with $\mathrm{C_1}$–$\mathrm{C_3}$ alkanes, $\mathrm{C_2}$–$\mathrm{C_6}$ alkenes, and $\mathrm{C_1}$–$\mathrm{C_3}$ alcohols, consistent with the high stability of these cluster ions. However, interesting reactivity is observed with sec-butylamine. After rapid condensation of two molecules of sec-butylamine onto the cluster ion, deamination and dehydrogenation of a third reagent molecule is observed [reaction (6)]. This reaction is competitive with condensation of a third sec-butylamine molecule onto the cluster bis-ligand ion [reaction (7)]:



(6)

(7)

For $n = 3$, reaction (6) accounts for 10% of the products, whereas for $n = 5$, reaction (6) accounts for 65% of the products. In contrast, Ag^+ reacts with sec-butylamine via rapid hydride abstraction to form AgH, with a minor amount of condensation product (<2%) also produced [reactions (8) and (9)].



(8)

(9)

Observation of reaction (6) indicates $D^0(\mathrm{Ag}_n\mathrm{L}_2^+\text{-butadiene}) > 1.73$ eV ($n = 3,5$; L = sec-butylamine). The enhanced reactivity of the cluster bis-ligand species over the bare cluster can be explained by a reduction in symmetry of the cluster ion. Alternatively, coupling of the ligands on the surface of the cluster may be occurring; however, this seems unlikely given the fact that sec-butylamine is a saturated species.

CONCLUSION

Laser desorption from metal oxides has been demonstrated to be an excellent technique for the production of small, bare metal cluster ions. Studies of Zn_2^+ show rapid displacement of zinc in reactions with alcohols and alkenes, which is consistent with the weak bonding in Zn_2^+. A simple valence electron picture of the bonding in Zn_2^+ indicates a formal bond order of one-half. Ag_3^+ does not undergo collision-induced dissociation at lab energies up to 100 eV, consistent with previous studies which indicate unusually high stability for Ag_3^+. Ag_5^+ fragments to form only Ag_3^+ upon collisional activation. In an interesting reaction, $Ag_3L_2^+$ and $Ag_5L_2^+$ (L = sec-butylamine) are observed to react with sec-butylamine through deamination and dehydrogenation. These results suggest that ligand-modified cluster chemistry may very well be as interesting as the size and composition dependent chemistry emerging from these studies.

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[1] For reviews on cluster research see: (a) Faraday Symp. Chem. Soc. **14** (1980); (b) Ber. Bunsenges. Phys. Chem. **88** (3) (1984); (c) Surf. Sci. **156** (1985); (d) M. D. Morse, Chem. Rev. **86** (1986).

[2] R. E. Smalley, *Comparison of Ab-Initio Quantum Chemistry with Experiment*, edited by R. J. Bartlett (Reidel, Dordrecht, 1985).

[3] (a) M. F. Geusic, M. D. Morse, and R. E. Smalley, J. Chem. Phys. **82**, 590 (1985); (b) M. F. Geusic, M. D. Morse, S. C. O'Brien, and R. E. Smalley, Rev. Sci. Instrum. **56**, 2123 (1985).

[4] D. M. Kolb, *Matrix Isolation Spectroscopy*, edited by A. J. Barnes, A. Muller, Orville-Thomas, and R. Gaufres (Reidel, Dordrecht, 1981).

[5] (a) R. B. Freas and D. P. Ridge, J. Am. Chem. Soc. **106**, 825 (1984); (b) D. B. Jacobson and B. S. Freiser, *ibid.* **106**, 4623 (1984).

[6] (a) L. Hanley and S. L. Anderson, Chem. Phys. Lett. **122**, 410 (1985); (b) R. B. Freas and J. E. Campana, J. Am. Chem. Soc. **108**, 4660 (1986); (c) P. B. Armentrout, S. K. Loh, and K. M. Ervin, *ibid.* **106**, 1161 (1984).

[7] B. S. Freiser, Talanta **32**, 697 (1985).

[8] J. M. Alford, P. E. Williams, D. J. Trevor, and R. E. Smalley, Int. J. Mass Spec. Ion Proc. **74**, 1 (1986).

[9] J. M. Alford, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley, J. Phys. Chem. **90**, 4480 (1986).

[10] M. Moini and J. R. Eyler, Chem. Phys. Lett. (submitted).

[11] D. A. Weil and C. L. Wilkins, J. Am. Chem. Soc. **107**, 7316 (1985).

[12] S. Ghaderi and D. P. Littlejohn, Fourier Transform Mass Spectrometry Using a Multiple Cell Configuration, presented at the 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego, California May 26–31, (1985).

[13] M. B. Comisarow, G. Parisod, and V. Grassi, Chem. Phys. Lett. **57**, 413 (1978).

[14] R. B. Cody, R. C. Burnier, and B. S. Freiser, Anal. Chem. **54**, 96 (1982).

[15] M. S. Ahmed and R. C. Dunbar, J. Am. Chem. Soc. **109**, 3215 (1987).

[16] Supplementary thermochemical information taken from: H. M. Rosenstock, D. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data **6**, Suppl. I (1977).

[17] (a) P. J. Hay, T. H. Dunning, Jr., and R. C. Raffenetti, J. Chem. Phys. **65**, 2679 (1976); (b) H. Tatewaki, M. Tomonari, and T. Nakamura, *ibid.* **82**, 5608 (1985).

[18] W. Schroeder, H. Wiggenhauser, W. Schrittenlacher, and D. M. Kolb, J. Chem. Phys. **86**, 1147 (1987).

[19] K. D. Carlson and K. R. Kuschnir, J. Phys. Chem. **68**, 1566 (1964).

[20] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **13**, 49 (1977).

[21] K. Ervin, S. K. Loh, N. Aristov, and P. B. Armentrout, J. Phys. Chem. **87**, 3593 (1983).

[22] D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987).

[23] B. S. Larsen, R. B. Freas, and D. P. Ridge, J. Phys. Chem. **88**, 6014 (1984).

[24] J. E. Bartmess and J. Kester, Inorg. Chem. **23**, 1877 (1984).

[25] I. Katakuse, T. Ichihara, Y. Fujita, T. Matsuo, T. Sakurai, and H. Matsuda, Int. J. Mass Spec. Ion Proc. **74**, 33 (1986).

[26] P. Fayet and L. Woste, Surf. Sci. **156**, 134 (1985).

[27] W. Andreoni and J. L. Martins, Surf. Sci. **156**, 635 (1985).

[28] J. A. Howard, K. F. Preston, and B. Mile, J. Am. Chem. Soc. **103**, 6226 (1981).

[29] H. Kang and J. L. Beauchamp, J. Phys. Chem. **89**, 3364 (1985).

[30] L. Hanley and S. L. Anderson, Chem. Phys. Lett. **122**, 410 (1985).

[31] S. K. Loh, D. A. Hales, and P. B. Armentrout, Chem. Phys. Lett. **129**, 527 (1986).

[32] T. Su and M. T. Bowers, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. 1, pp. 83–118.

[33] M. Bensimon and R. Houriet, Int. J. Mass Spec. Ion Proc. **72**, 93 (1986).

[34] (a) M. Mautner, J. Am. Chem. Soc. **104**, 5 (1982); (b) L. Sallans, K. R. Lane, R. R. Squires, and B. S. Freiser, *ibid.* **107**, 4379 (1985).