Collision-induced dissociation processes of Nb_4^+ and Fe_4^+: Fission vs evaporation

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Despite the extensive effort devoted to research on gas-phase metal clusters, quantitative thermodynamic data on such species are scarce. Such information is key to understanding and predicting the physical and chemical properties of clusters. Presently, bond energies are available primarily for transition metal[1] dimers[2] and some trimers,[3] although ionization potentials have been measured for a broader range of sizes.[4] In this work, we illustrate the use of guided ion beam mass spectrometry for obtaining this type of thermodynamic data on transition metal clusters. Nb_n^+ and Fe_n^+ are chosen as illustrative of metals on the left and right sides of the periodic table and because they should have very different thermodynamic properties, $D_0^0(Nb_2) = 5.0 \pm 0.4$ eV and $D_0^0(Fe_2) = 1.1 \pm 0.2$ eV.[2,5,6]

Experiments were conducted with a new ion beam instrument[7] designed to measure the energy dependence of metal cluster ion reactions. The source is a modified version of one previously described[8] which uses laser vaporization, condensation by helium, and a supersonic expansion to create thermalized cluster ions. Collision-induced dissociation (CID) takes place under single collision conditions within an octopole ion beam guide to ensure efficient product collection.[7]

CID cross sections of Nb_4^+ with Xe are shown in Fig. 1(a). Table I lists the endoergicities of all possible CID processes with some values based on our CID results for smaller Nb and Fe cluster ions. The total cross section rises smoothly to reach a constant value at high energies, indicating efficient product collection. The lowest energy process is symmetric cleavage of the cluster to form $Nb_2^+ + Nb_2$, at 4.3 ± 0.3 eV. Atom loss, $Nb_3^+ + Nb$, cannot occur until 5 eV. This channel becomes dominant above 10 eV, consistent with high energy ($\geqslant$10 eV) photodissociation studies of slightly larger Nb clusters.[9] Nb^+ formation is much less probable. Its threshold suggests that Nb^+ comes primarily from dissociation of the Nb_2^+ product. Importantly, *the "most probable" process is highly energy dependent*, i.e., the relative thermodynamic stability of the dimer and trimer ions is not reflected by the branching ratio at elevated kinetic energies.

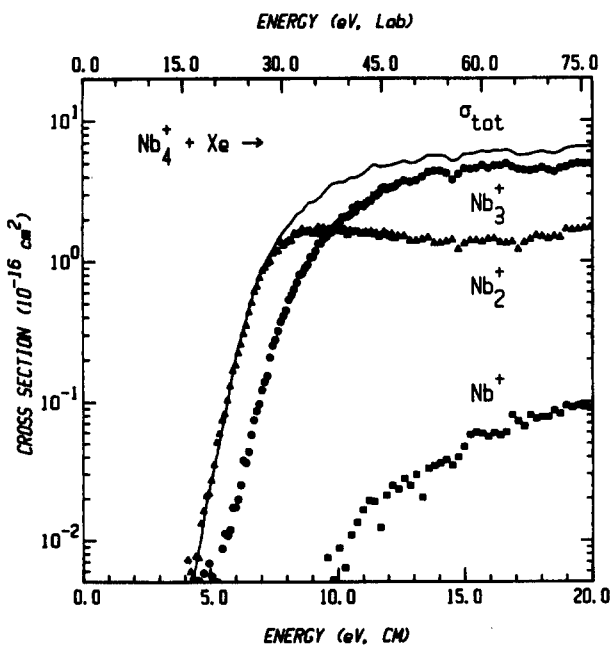

FIG. 1. (a) Collision-induced dissociation of Nb_4^+ by Xe. (b) Collision-induced dissociation of Fe_4^+ by Xe. Cross sections are shown as a function of kinetic energy in the center-of-mass frame (lower x axis) and the laboratory frame (upper x axis).

Figure 1(b) shows results for $Fe_4^+ + Xe$. Again, the total cross section behaves smoothly and reaches a constant value at high energies. Unlike Nb_4^+, the lowest energy process is formation of Fe_3^+. The fission process, $Fe_2^+ + Fe_2$, lies only 0.5 eV higher in energy, Table I, but the threshold observed for Fe_2^+ is near the thermodynamic limit for $Fe_2^+ + 2Fe$, 3.4 eV. Similarly, Fe^+ is observed near the threshold for evaporation, $Fe^+ + 3Fe$. This behavior is similar to that noted in photodissociation studies of iron cluster ions.[5] While we cannot strictly rule out formation of neutral molecular fragments (since excess energy may be carried away as product kinetic energy), this conflicts with the observation that $\sigma(Fe_3^+)$ declines as $\sigma(Fe_2^+)$ rises, consistent with the process $Fe_3^+ \rightarrow Fe_2^+ + Fe$.

The results described here are typical of the behavior of larger niobium and iron cluster ions. CID studies of Nb_n^+ ($n = 2$–6) continue to show fragmentation to molecular and atomic products, while Fe_n^+ studies ($n = 2$–10) show dissociation exclusively via sequential atom loss.[10] This behavior is consistent with the idea that metals like Nb can form strong bonds via multiple d–d bonding,[11] $D^0(Nb_2) \simeq 5.0$ eV and $D^0(Nb_2^+) \simeq 5.9$ eV.[10] In contrast, re-

TABLE I. Collision induced dissociation endoergicities (eV).[a]

Process			M = Nb	Fe
M_4^+	→	$M_3^+ + M$	5.0	1.8
	→	$M_2^+ + M_2$	4.3	2.3
	→	$M_2^+ + 2M$	9.3	3.4
	→	$M^+ + M_3$	$\simeq$5.5	3.3
	→	$M^+ + M_2 + M$	10.3	4.9
	→	$M^+ + 3M$	16.0	6.0

[a] Values are from preliminary analysis of CID data presented here and of data for smaller cluster ions. Values of $D^0(Nb_2) = 5.0$ eV and $D^0(Fe_2) = 1.1$ eV are also assumed (Refs. 2 and 6).

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sults for iron are consistent with the weak Fe_2 bond ($D^0 \simeq 1.1$ eV), thought to be predominantly a 4*s*–4*s* interaction.[12] The Fe^+–Fe bond is much stronger ($D^0 \simeq 2.7$ eV)[5,6] although considerably weaker than those in the Nb system. It will be interesting to see whether the observed differences between these clusters are prototypical for metals on the left and right side of the Periodic Table. These differences are very evident in reactivity experiments in progress in our laboratory. Such studies provide considerable qualitative and *quantitative* insight into metal–metal and metal–ligand bonding across the transition metal series.

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