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# Energetics of the manganese trimer and tetramer ions

Akira Terasaki, Shinichirou Minemoto,<sup>a)</sup> and Tamotsu Kondow<sup>b)</sup>

Cluster Research Laboratory, Toyota Technological Institute, in East Tokyo Laboratory, Genesis Research Institute, Inc., 717-86 Futamata, Ichikawa, Chiba 272-0001, Japan

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The photodissociation processes of the manganese cluster ions  $Mn_n^+$  ( $n=3$  and  $4$ ) were investigated in the visible and near-infrared photon-energy ranges. The threshold energies were determined for the two-atom-loss channels by measurements of the spectra of the partial photodissociation cross sections. The binding energies of  $Mn_n^+$  ( $n=3$  and  $4$ ) were obtained by using these threshold energies and the known bond dissociation energy of  $Mn_2^+$ . The bond dissociation energies of  $Mn_3^+$ ,  $D_0(Mn_2^+\cdots Mn)$ , and  $Mn_4^+$ ,  $D_0(Mn_3^+\cdots Mn)$ , were determined to be  $0.83\pm 0.05$  and  $1.04\pm 0.07$  eV, respectively. Thus the binding energies (per atom) of  $Mn_3^+$  and  $Mn_4^+$  turned out to be  $0.74\pm 0.03$  and  $0.82\pm 0.05$  eV, respectively. These findings show that the interaction between manganese atoms is exceptionally weak, compared with other transition-metal cluster ions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1509064]

## I. INTRODUCTION

It is known that manganese forms very weakly bound systems in the two extremes of the size range, i.e., both in the bulk and in the diatomic molecule. Among the bulk transition metals, it has the smallest bulk modulus ( $5.96 \times 10^{10}$  N/m<sup>2</sup>) and the lowest cohesive energy (2.92 eV/atom).<sup>1</sup> On the other hand, the binding energy of the manganese dimer  $D_0(Mn\cdots Mn)$  is reported by thermodynamic measurements to vary from  $0.1\pm 0.1$  to  $0.56\pm 0.26$  eV depending on the models employed for analyses;  $0.44\pm 0.3$  eV is the currently accepted estimate.<sup>2-4</sup> Although the uncertainty is large, it is clearly much lower than those of the other homonuclear diatomics of  $3d$  transition-metal elements, which are in the range between 1.1 and 2.5 eV.<sup>3</sup> The weak interaction between manganese atoms arises from the electronic configuration of the atom. The manganese atom has a fully occupied  $4s$  shell and a half-filled  $3d$  shell,  $3d^5 4s^2$  configuration. This configuration makes the energy of the promotion,  $3d^5 4s^2 \rightarrow 3d^6 4s^1$ , very high (2.14 eV),<sup>5</sup> which is necessary to form a covalent bond. Therefore, the ground-state electronic configuration of the dimer is considered to be  $(3d)^{10}(4s\sigma_g)^2(4s\sigma_u^*)^2$  with its formal bond order of zero, which suggests a van der Waals-type interaction with a nonbonding nature of  $3d$  orbitals. The weak bond in the dimer is consistent with other experimental observations, which include the long bond length (3.4 Å) (Refs. 6 and 7) and the low vibrational frequency ( $59-76$  cm<sup>-1</sup>) (Ref. 8) and with theoretical studies (Refs. 9-17).

The manganese dimer ion  $Mn_2^+$  is also weakly bound. The bond dissociation energy of  $Mn_2^+$ ,  $D_0(Mn^+\cdots Mn)$ , has been determined by experiments of collision-induced dissociation<sup>18,19</sup> and photodissociation spectroscopy.<sup>20</sup> The most reliable dissociation energy is obtained to be 1.39 eV (Refs. 20 and 21) by careful analysis of the photodissociation

threshold, which takes into account the internal energy of the dimer ion produced by the electron impact of  $Mn_2(CO)_{10}$ . This binding energy of the positively charged dimer is much lower than those of the other  $3d$  transition metals, except for the comparable value of  $Cr_2^+$  ( $1.30\pm 0.06$  eV).<sup>22</sup> It is understood that the ground-state electronic configuration is  $(3d)^{10}(4s\sigma_g)^2(4s\sigma_u^*)^1$  with the formal bond order of  $1/2$ ,<sup>11,21</sup> since the energy of the promotion,  $3d^5 4s^1 \rightarrow 3d^6 4s^0$ , is high (1.81 eV) (Ref. 23) in a manganese cation  $Mn^+$ . The electronic structure of  $Mn_2^+$  has recently been studied by the UV-visible optical absorption spectroscopy and analyzed by quantum-chemical calculation.<sup>24</sup>

These studies show that manganese is weakly bound both in the dimer (ion) and in the bulk when it is compared with the corresponding systems of other transition-metal elements. However, the binding energy of a manganese assemble certainly increases from that of the dimer to the bulk cohesive energy. This raises a question about the size evolution of the bonding mechanism of the constituent atoms of manganese clusters. In this regard, the secondary-ion mass spectrum (SIMS) of manganese cluster ions  $Mn_n^+$  has been measured and revealed that the abundant sizes (magic numbers) in the mass spectrum coincide with those of rare-gas cluster ions; the magic numbers implied a van der Waals nature of the bonding in the size range below  $n=60$ .<sup>25</sup> In the present study, the binding energies of the manganese ions of trimer,  $Mn_3^+$ , and tetramer,  $Mn_4^+$ , were determined by the photodissociation experiments, where the threshold energies were measured for the dissociation channels being switched. The binding energies per atom of  $Mn_3^+$  and  $Mn_4^+$  were found to be as small as that of  $Mn_2^+$ .

## II. EXPERIMENTAL PROCEDURES

The experiments were performed by using a tandem time-of-flight (TOF) mass spectrometer equipped with a tunable pulsed laser for photodissociation,<sup>24,26</sup> which is capable of irradiation of the laser pulse to a size-selected primary cluster ion and successive mass analysis of photofragment ions. Manganese cluster ions were generated by the laser-

<sup>a)</sup>Present address: Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, Japan.

<sup>b)</sup>Electronic mail: kondow@mail.cluster-unet.ocn.ne.jp

vaporization technique. The second harmonics of a pulsed Nd:YAG laser (GCR-11, Spectra Physics) operated at 10 Hz was focused on a rotating metal disk mounted in a cluster source. A manganese plate fabricated by the electrolytic refining was used for the sample disk. A helium gas mixed with 10 vol. % argon gas was used as a carrier gas. The temperature of the cluster-growth room was kept at  $210 \pm 20$  K by a careful flowing of a cold nitrogen gas vaporized from liquid nitrogen through a pipe attached to the cluster-growth room. Both the introduction of an argon gas to the carrier gas and the cooling of the cluster-growth room favored the formation of cluster ions larger than trimer. The cluster ions thus produced were extracted in the perpendicular direction by a pulsed electric field into a TOF mass spectrometer, where the cluster ions traveled at a kinetic energy of 1.6 keV. After mass selection, cluster ions of a target size, either  $\text{Mn}_3^+$  or  $\text{Mn}_4^+$  in the present experiments, were irradiated with a tunable laser pulse from an optical parametric oscillator (OPO; MOPO-730, Spectra Physics). The photon energy was varied from 1.00 (1240) to 2.79 eV (445 nm) with a laser-tuning gap between 1.65 (750) and 1.82 eV (680 nm). The intensity of the laser pulse was kept below  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  in order to ensure the single-photon process, which was monitored during the experiment. The photofragment and the residual primary ions were further mass-analyzed by the secondary TOF mass spectrometer equipped with a reflectron and detected by a microchannel plate (F4655, Hamamatsu). The resulting TOF spectrum was digitized and stored in a transient digitizer (DM2350, Iwatsu) and was transferred to a personal computer (PC-9801VX, NEC) for further data processing. Typically, 300 data sets were accumulated to obtain each TOF spectrum.

The photodissociation cross sections were obtained as follows: The yield of each photofragment ion of size  $m$ ,

$$Y(\text{Mn}_m^+) = I(\text{Mn}_m^+) / \sum_{k=1}^n I(\text{Mn}_k^+), \quad (1)$$

was calculated from the intensities of the primary ion,  $I(\text{Mn}_n^+)$ , and the photofragment ions,  $I(\text{Mn}_k^+)$  ( $1 \leq k \leq n-1$ ). By using the measured intensity of the dissociation laser (or the photon flux  $F$ ), the partial photodissociation cross section was obtained:  $\sigma_m = Y(\text{Mn}_m^+) / F$  for each dissociation channel. Here the dissociation laser beam, the diameter of which was as large as 6 mm, was assumed to overlap completely with the primary cluster-ion beam, which was confirmed in the experiment. The uncertainty in the absolute cross section thus obtained was estimated to be  $\pm 50\%$  of the average value, where a main source of error was an occasional incomplete overlap between the laser pulse and ion bunch. On the other hand, the relative values had statistical errors of  $\pm 20\%$  or less, which were evaluated at several photon energies by repeating the measurements.

### III. RESULTS

Figure 1(a) shows the partial photodissociation cross sections of  $\text{Mn}_3^+$ , from which  $\text{Mn}_2^+$  (one-atom loss) and/or  $\text{Mn}^+$  (two-atom loss) were produced. The dominant photofragment ion was  $\text{Mn}_2^+$  at photon energies below about 2

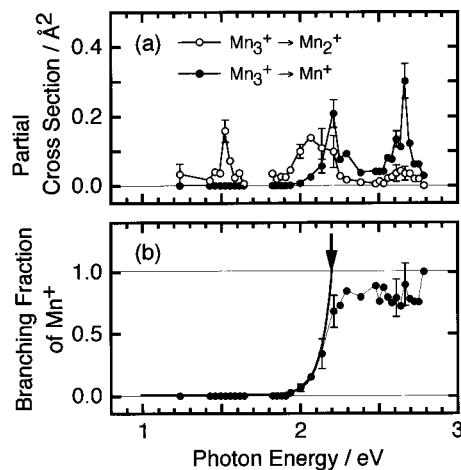


FIG. 1. (a) Spectra of the partial photodissociation cross sections of  $\text{Mn}_3^+$ : open (solid) circles are for the dissociation channel to  $\text{Mn}_2^+$  ( $\text{Mn}^+$ ). (b) Branching fraction of the  $\text{Mn}^+$  channel as a function of the photon energy. The thick solid curve represents the internal-energy distribution of primary  $\text{Mn}_3^+$ , which explains the onset behavior. The arrow indicates the threshold energy of the  $\text{Mn}^+$  formation from  $\text{Mn}_3^+$ .

eV, whereas the major photofragment ion was switched to  $\text{Mn}^+$  at higher energies. As shown in Fig. 1(b), the branching fraction of the two-atom loss exhibited a rise at 1.9 eV and leveled off at 2.2 eV. The gradual increase in the  $\text{Mn}^+$  formation is due to the internal energies of the primary cluster ions; internally hot cluster ions dissociate at photon energies lower than cold ones. The atomization energy  $E_b(\text{Mn}_3^+)$  of  $\text{Mn}_3^+$  was determined by this threshold energy, as will be described in the following section. The photodissociation spectrum also exhibited resonance structures corresponding to excited electronic states of  $\text{Mn}_3^+$ . The analysis of the electronic spectrum requires high-level quantum chemical calculations and will be reported in a separate paper.<sup>27</sup>

Figure 2 shows the results on  $\text{Mn}_4^+$ , where three features are discernible. First, the trimer ion  $\text{Mn}_3^+$  was produced as the dominant photofragment ion even at a photon energy as low as 1 eV. This result simply places an upper limit on the bond dissociation energy of  $\text{Mn}_4^+$ , i.e.,

$$D_0(\text{Mn}_3^+ \cdots \text{Mn}) < 1.00 \text{ eV} + E_{\text{int}}(\text{Mn}_4^+), \quad (2)$$

where  $E_{\text{int}}(\text{Mn}_4^+)$  represents the internal energy of the primary  $\text{Mn}_4^+$ . Second, at higher energies,  $\text{Mn}_2^+$  was produced predominantly via two-atom loss. The branching fraction of the two-atom loss, shown in Fig. 2(b), started to increase at about 1.2 eV and grows sharply toward 1.9 eV. This behavior is similar to that observed for  $\text{Mn}_3^+$  except that the branching fraction changed more slowly as the photon energy increased. It is reasonable, because the internal energy of  $\text{Mn}_4^+$  is higher than that of  $\text{Mn}_3^+$  at the same temperature due to the larger internal degrees of freedom. The threshold energy determined in the following section corresponds to the dissociation energy,  $D_0(\text{Mn}_2^+ \cdots 2\text{Mn})$ , liberating two Mn atoms from  $\text{Mn}_4^+$ . Finally, in the present photon-energy range up to 2.79 eV, the monomer fragment ion  $\text{Mn}^+$  was not observed. This fact places a lower limit on the atomization energy of  $\text{Mn}_4^+$ ,  $E_b(\text{Mn}_4^+)$ :

$$E_b(\text{Mn}_4^+) > 2.79 \text{ eV} + E_{\text{int}}(\text{Mn}_4^+). \quad (3)$$

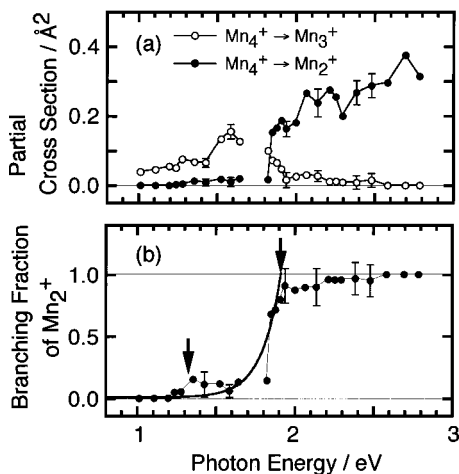


FIG. 2. (a) Spectra of the partial photodissociation cross sections of  $\text{Mn}_4^+$ : open (solid) circles are for the dissociation channel to  $\text{Mn}_3^+$  ( $\text{Mn}_2^+$ ). (b) Branching fraction of the  $\text{Mn}_2^+$  channel as a function of the photon energy. The thick solid curve represents the internal-energy distribution of primary  $\text{Mn}_4^+$ , which explains the onset behavior. The right arrow indicates the threshold energy of the  $\text{Mn}_2^+$  formation by liberating two neutral atoms from  $\text{Mn}_4^+$ . The left arrow indicates that of the  $\text{Mn}_2^+$  formation by  $\text{Mn}_2^+$  release, which was presumed.

## IV. DISCUSSION

### A. Trimer ion

The onset behavior of the  $\text{Mn}^+$  formation from  $\text{Mn}_3^+$  is analyzed in order to obtain the energetics of  $\text{Mn}_3^+$ . The gradual rise of the  $\text{Mn}^+$  branching fraction in Fig. 1(b) indicates that the primary trimer ions have an internal-energy distribution at finite temperature as determined by the cluster-growth room; internally hot cluster ions dissociate at photon energies lower than cold ones. Also the branching fraction changes smoothly and monotonically without any resonance structures. This finding is consistent with the conjecture that  $\text{Mn}^+$  is produced by predissociation rather than direct dissociation along a repulsive potential energy surface in the excited state. In this statistical process the two-body dissociation process of  $\text{Mn}_3^+$  should proceed not to the neutral-dimer release,  $\text{Mn}_2 + \text{Mn}^+$ , but to the neutral-monomer evaporation,  $\text{Mn}_2^+ + \text{Mn}$ , since the ionization potential of Mn atom is higher than that of  $\text{Mn}_2$ .<sup>20</sup> Therefore, in this particular dissociation channel of  $\text{Mn}_3^+$  to  $\text{Mn}^+$ , the counterneutral species are two Mn atoms via sequential loss of Mn atoms.

In the mechanism of the photodissociation process mentioned above, the atomization energy of  $\text{Mn}_3^+$ ,  $E_b(\text{Mn}_3^+)$ , is evaluated as follows: Suppose that the primary cluster ions  $\text{Mn}_3^+$  are populated in internally hot levels according to the Boltzmann distribution law, which gives the population  $P(E_{\text{int}}) = \exp[-E_{\text{int}}/\langle E_{\text{int}} \rangle] / \langle E_{\text{int}} \rangle$ , with an average internal energy  $\langle E_{\text{int}} \rangle$ . Once  $\text{Mn}_3^+$  absorbs a photon with energy  $E_p$ , it is dissociated to  $\text{Mn}^+$  if  $E_p + E_{\text{int}} > E_b(\text{Mn}_3^+)$ , while it remains to be  $\text{Mn}_2^+$  otherwise. Therefore, the branching fraction  $R(E_p)$  of  $\text{Mn}^+$  is the integrated population over the primary cluster ions hot enough to have  $E_{\text{int}} > E_b(\text{Mn}_3^+) - E_p$ . This gives rise to the following equation for explaining the onset behavior of the branching fraction of  $\text{Mn}^+$ :

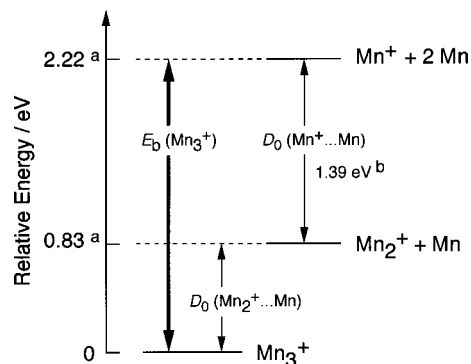


FIG. 3. Energy diagram of the photodissociation process of  $\text{Mn}_3^+$ . The thick arrow indicates the experimentally determined threshold. (a) Present work. (b) From Ref. 21.

$$R(E_p) = \int_{E_{\text{th}} - E_p}^{\infty} dE_{\text{int}} P(E_{\text{int}}),$$

$$= \exp[(E_p - E_{\text{th}}) / \langle E_{\text{int}} \rangle], \quad (4)$$

where  $E_{\text{th}} = E_b(\text{Mn}_3^+)$ . By applying this equation to the data in Fig. 1(b), it is obtained that  $E_b(\text{Mn}_3^+) = 2.22 \pm 0.05$  eV and that  $\langle E_{\text{int}} \rangle = 0.06 \pm 0.01$  eV as shown by the thick solid curve. The average internal energy thus obtained agrees with that estimated by the temperature of the primary  $\text{Mn}_3^+$  in equilibrium with the cluster-growth room at  $T = 210$  K, where  $\langle E_{\text{int}} \rangle = skT$ , with  $s$  representing the internal degrees of freedom ( $3n - 6$ ) and  $k$  the Boltzmann constant. This agreement supports the present interpretation of the onset behavior. The energetics of  $\text{Mn}_3^+$  is summarized in Fig. 3. The bond dissociation energy of  $\text{Mn}_3^+$ ,  $D_0(\text{Mn}_2^+ \cdots \text{Mn})$ , is further deduced to be  $0.83 \pm 0.05$  eV, as the bond dissociation energy of the dimer ion,  $D_0(\text{Mn}^+ \cdots \text{Mn})$ , is reported to be 1.39 eV.<sup>21</sup>

The electronic states of the photofragments produced at the atomization threshold were assigned to the ground states:  $\text{Mn}^+(^7S)$  and  $\text{Mn}(^6S)$ . Since the first excited state  $^5S$  of  $\text{Mn}^+$  lies at 1.17 eV above  $^7S$ ,<sup>20</sup> it requires 2.56 eV for  $\text{Mn}_2^+$  to dissociate into  $\text{Mn}^+(^5S)$  and  $\text{Mn}(^6S)$ . Therefore, it is not allowed energetically for  $\text{Mn}_3^+$  to produce excited-state  $\text{Mn}^+(^5S)$  at the threshold photon energy of 2.22 eV. For a similar reason, the first excited state  $^6D$  of Mn is not produced, which is 2.14 eV higher in energy than the ground state  $^6S$ .<sup>5</sup> Note that the photodissociation occurs in a spin-conserved manner; the ground state of  $\text{Mn}_3^+$  has been shown to have a total spin  $S = 8$ ,<sup>27</sup> while the products have  $S = 3$  and  $5/2$  for  $\text{Mn}^+(^7S)$  and  $\text{Mn}(^6S)$ , respectively. In other words, ferromagnetic spin coupling between  $\text{Mn}^+(^7S)$  and two  $\text{Mn}(^6S)$  forms the high-spin ground state of  $\text{Mn}_3^+$ .

### B. Tetramer ion

The threshold energy for  $\text{Mn}_4^+$  to dissociate into  $\text{Mn}_2^+$  was observed to be about 1.9 eV as shown in Fig. 2(b). The onset of the branching fraction of  $\text{Mn}_2^+$  is analyzed by the same model employed in the analysis of the  $\text{Mn}_3^+$  data, which takes into account the internal energy distribution of the primary cluster ions. By applying Eq. (4) to these onset data, it is obtained that  $E_{\text{th}} = 1.92 \pm 0.05$  eV and that  $\langle E_{\text{int}} \rangle$

$=0.12\pm0.03$  eV as shown by the thick solid curve in Fig. 2(b). The average internal energy agrees with that estimated for  $\text{Mn}_4^+$  with six internal degrees of freedom at the cluster-source temperature of 210 K. The threshold energy  $E_{\text{th}}$  would correspond either to the sequential loss of two atoms,  $\text{Mn}_2^+ + 2\text{Mn}$ , or to the neutral-dimer release,  $\text{Mn}_2^+ + \text{Mn}_2$ , where the latter process requires energy less by the bond dissociation energy,  $D_0(\text{Mn}\cdots\text{Mn})$ , of the neutral dimer. The present threshold is attributable to the former process, because the branching fraction is almost unity at  $E_{\text{th}}$  and there was observed no further increase in the  $\text{Mn}_2^+$  formation at higher photon energies.

Here we should mention the lifetimes of the excited states in the predissociation processes, because the clusters require an internal energy above their dissociation threshold to be dissociated within the time scale of the experiment. The dissociation rate is estimated by the statistical model based on the Rice–Ramsperger–Kassel (RRK) theory. In this model the dissociation rate  $k(E)$  at the internal energy  $E$  of the cluster is expressed by  $k(E) = \nu [(E - D_0)/E]^s$ , where  $\nu$  is the frequency of the characteristic modes,  $s$  the number of the vibrational degrees of freedom, and  $D_0$  the bond dissociation energy. On the assumption that the mode frequency  $\nu$  is  $100\text{ cm}^{-1}$  as found for the vibrational frequency of the manganese dimer in rare-gas matrices,<sup>8</sup> the excess energies necessary for the cluster ions to dissociate before the product mass analysis (within  $20\ \mu\text{s}$  in the present experimental condition) are estimated to be  $1.2 \times 10^{-4} D_0$  and  $2.7 \times 10^{-2} D_0$  for  $\text{Mn}_3^+$  and  $\text{Mn}_4^+$ , respectively. The effect of the excited-state lifetime is negligible in the case of the trimer ions, because this excess energy ( $<10^{-3}$  eV) is much less than the uncertainties (0.05 eV) in the binding energies obtained. For the tetramer ions, on the other hand, the overestimate of the result should be compensated for, since the required excess energy is comparable with the experimental error.

Due to the finite excited-state lifetime, the present threshold energy  $E_{\text{th}}$  ( $1.92 \pm 0.05$  eV) represents the minimum energy required for  $\text{Mn}_4^+$  to produce  $\text{Mn}_2^+$  in a time scale short enough before the fragment mass analysis and overestimates the actual dissociation energy,  $D_0(\text{Mn}_2^+\cdots 2\text{Mn})$ , by about 0.05 eV. Thus, one obtains that  $D_0(\text{Mn}_2^+\cdots 2\text{Mn}) = 1.87 \pm 0.05$  eV for the dissociation energy of  $\text{Mn}_4^+$  liberating two atoms. The energetics of  $\text{Mn}_4^+$  is summarized in Fig. 4. The other parameters are calculated as follows:  $D_0(\text{Mn}_3^+\cdots \text{Mn}) = D_0(\text{Mn}_2^+\cdots 2\text{Mn}) - D_0(\text{Mn}_2^+\cdots \text{Mn}) = 1.04 \pm 0.07$  eV and  $E_b(\text{Mn}_4^+) = E_b(\text{Mn}_3^+) + D_0(\text{Mn}_3^+\cdots \text{Mn}) = 3.26 \pm 0.09$  eV. Note that these energies satisfy the upper bound of  $D_0(\text{Mn}_3^+\cdots \text{Mn})$  and the lower bound of  $E_b(\text{Mn}_4^+)$  given experimentally by Eqs. (2) and (3), respectively, where the internal energy  $E_{\text{int}}(\text{Mn}_4^+)$  of  $\text{Mn}_4^+$  was estimated to be 0.12 eV.

The electronic state of  $\text{Mn}_4^+$  has been investigated by first-principles calculations. It is predicted that a high-spin state with  $S=21/2$  and a lower-spin state with  $S=9/2$  are nearly degenerate within 0.05 eV in the total-energy difference.<sup>28</sup> In the sequential cluster-growth process in a laser vaporization cluster source, the total spin is conserved from reactants to a product.<sup>29</sup> Since the ground spin states of  $\text{Mn}_2^+$  and Mn are  $S=11/2$  (Refs. 24 and 30) and  $5/2$ , respec-

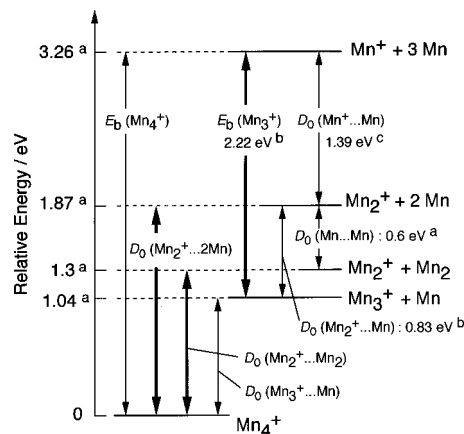


FIG. 4. Energy diagram of the photodissociation process of  $\text{Mn}_4^+$ . The thick arrows indicate the experimentally determined thresholds. (a) Present work. (b) Present work on  $\text{Mn}_3^+$ . (c) From Ref. 21.

tively, the spin-allowed  $\text{Mn}_4^+$  product is in  $S=21/2$ ,  $11/2$ , or  $1/2$ . Therefore, it is likely that the high-spin state ( $S=21/2$ ) is produced preferentially over the lower-spin state ( $S=9/2$ ). The photodissociation of  $\text{Mn}_4^+$  ( $S=21/2$ ), in reverse, proceeds in a spin-conserved manner and produces photofragments in the ground electronic states:  $\text{Mn}_3^+$  ( $S=8$ ) +  $\text{Mn}$  ( $S=5/2$ ),  $\text{Mn}_2^+$  ( $S=11/2$ ) +  $2\text{Mn}$  ( $S=5/2$ ), and  $\text{Mn}^+$  ( $S=3$ ) +  $3\text{Mn}$  ( $S=5/2$ ).

Finally, we would like to mention the bond dissociation energy of the neutral dimer,  $D_0(\text{Mn}\cdots\text{Mn})$ . In spite of the long history of discussion, it is given only with a very large uncertainty:  $D_0(\text{Mn}\cdots\text{Mn}) = 0.44 \pm 0.3$  eV.<sup>2-4</sup> In the present experiment on the tetramer ion, a slight onset of  $\text{Mn}_2^+$  signal from  $\text{Mn}_4^+$  is discernible at about 1.3 eV, although the signal-to-noise ratio is not good enough. This threshold could arise from the formation of  $\text{Mn}_2^+$  and  $\text{Mn}_2$ :  $D_0(\text{Mn}_2^+\cdots \text{Mn}_2) = 1.3$  eV. Then, it is presumable that  $D_0(\text{Mn}\cdots\text{Mn}) = 0.6 \pm 0.1$  eV, being given by the relationship  $D_0(\text{Mn}\cdots\text{Mn}) = D_0(\text{Mn}_2^+\cdots 2\text{Mn}) - D_0(\text{Mn}_2^+\cdots \text{Mn}_2)$ . In order to conclude it decisively, a low-temperature experiment would be able to distinguish more clearly the ( $\text{Mn}_2^+ + \text{Mn}_2$ ) process from the ( $\text{Mn}_2^+ + 2\text{Mn}$ ) signal originating from internally hot cluster ions.

Photodissociation experiments sometimes have difficulty in determining a bond dissociation energy from the photodissociation threshold of the monomer-release process. It is required that an excitation of a cluster can occur at the photon energies in the vicinity of the bond dissociation energy: otherwise, the threshold energy provides only the upper limit of the bond energy. The criteria have been discussed for interpretation of photodissociation thresholds as bond dissociation energies on several transition-metal dimer and trimer ions.<sup>31</sup> In the present experiments, on the other hand, an onset of the two-atom release was observed instead, where the onset energy was in the absorption-line profile of the cluster ion and the two-atom-loss channel took over smoothly from one-atom loss as the photon energy increased.

It should be noted that the threshold energy could be determined precisely because of these experimental conditions.

## V. CONCLUSIONS

The photodissociation experiments were performed on the manganese trimer and tetramer ions. The threshold energies were determined for the two-atom-loss channels by the analysis of the onset behaviors of the branching fraction on the basis of the model proposed. The model takes into account the contribution of the internally hot primary cluster ions dissociating below the actual dissociation threshold. RRK theory was used to evaluate the minimum excess energy required due to the finite excited-state lifetime. The threshold energies thus obtained were  $E_{\text{th}}(\text{Mn}_3^+ \rightarrow \text{Mn}^+ + 2\text{Mn}) = 2.22 \pm 0.05$  eV and  $E_{\text{th}}(\text{Mn}_4^+ \rightarrow \text{Mn}_2^+ + 2\text{Mn}) = 1.87 \pm 0.05$  eV. These results and the bond dissociation energy of  $\text{Mn}_2^+$  (1.39 eV) (Ref. 21) deduced the following parameters in their energetics. For the trimer ion,  $\text{Mn}_3^+$ , the bond dissociation energy  $D_0(\text{Mn}_2^+ \cdots \text{Mn})$  was obtained to be  $0.83 \pm 0.05$  eV. Its atomization energy  $E_b(\text{Mn}_3^+)$  was  $2.22 \pm 0.05$  eV or  $0.74 \pm 0.03$  eV/atom. For the tetramer ion  $\text{Mn}_4^+$ ,  $D_0(\text{Mn}_3^+ \cdots \text{Mn})$  was obtained to be  $1.04 \pm 0.07$  eV. The atomization energy  $E_b(\text{Mn}_4^+)$  was  $3.26 \pm 0.09$  eV or  $0.82 \pm 0.05$  eV/atom. In addition, the bond dissociation energy of the neutral dimer,  $D_0(\text{Mn} \cdots \text{Mn})$ , was found to be  $0.6 \pm 0.1$  eV on the assumption that the onset of the slight  $\text{Mn}_2^+$  signal from  $\text{Mn}_4^+$  at 1.3 eV would correspond to the neutral-dimer release. The binding energies per atom of the dimer through the tetramer ions thus obtained indicate their exceptionally weak binding among the  $3d$  transition-metal clusters and their ions. The weak binding of manganese atoms suggests a ferromagnetic nature as found in the dimer ion.<sup>24,30</sup>

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