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Multiphoton fragmentation spectra of zirconium and niobium cluster cations

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Abstract

The dissociation energies of the mass-selected zirconium dimer cation ($^{90}\text{Zr}_2^+$) and niobium cation clusters, Nb_2^+ and Nb_4^+ , were investigated using laser vaporization techniques coupled with time-of-flight (TOF) mass spectroscopy for production of jet-cooled cationic cluster beams. The selected cationic species were then fragmented by irradiation with an Nd:YAG-pumped (532 nm), tunable-pulsed PDL dye laser in the 15,500–18,500 cm^{-1} region. Dissociation energies were directly measured from a significant sharp rise in the spectral background as $D_0(^{90}\text{Zr}_2^+) = 4.18 \pm 0.01$, $D_0(\text{Nb}_2^+) = 5.94 \pm 0.01$, and $D_0(\text{Nb}_3^+ - \text{Nb}) = 5.994 \pm 0.004$ eV. We also estimate the first ionization energy of $^{90}\text{Zr}_2^+$ to be 5.82 ± 0.01 eV using the thermochemical cycle.

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Keywords: Multiphoton fragmentation; Zirconium; Niobium; Laser vaporization; Time-of-flight mass spectroscopy

1. Introduction

The ionic and neutral transition metal clusters have received special interest since advent of techniques such as laser vaporization of a solid target, supersonic cooling, mass-selected resonant two-photon ionization, laser-induced fluorescence, and collision-induced dissociation [1–35]. We focus here on examining the photofragmentation threshold for several transition metal cluster cations produced through laser vaporization. With existing particle counting techniques it is possible to detect cluster ions with near-unit efficiency and as a consequence, absorption spectra of a mass-selected cluster ion can be readily obtained using high peak intensity probe lasers. Both one and multiphoton absorption spectra and the dissociation energy limit can be studied at high sensitivity.

For a multiphoton process, a molecule with energy in excess of its lowest dissociation threshold can dissociate given enough time assuming that there exist no barriers in excess of the threshold. The probability or normalized intensity of fragment cluster ions is inversely proportional to the number of photons absorbed by the parent ion. Therefore, the possi-

ble lowest dissociation energy of the parent ion can be determined from the onset of the fairly sharp rise in the spectral background of the fragment ion when the multiphoton process changes from an n -photon process to an $(n - 1)$ -photon process. The number of the absorbed photons may be determined by observation of the dissociation fluence dependence at the high and low frequency regions of the observed threshold energy.

In the present work, we studied multiphoton fragmentation spectroscopy of mass-selected $^{90}\text{Zr}_2^+$ and Nb_n^+ , $n = 2, 4$. Only the multiphoton fragmentation spectra of the $^{90}\text{Zr}_2^+$, $\text{Nb}_3^+ - \text{Nb}$ cations, in the range of 15,500–18,500 cm^{-1} , exhibit a sharp rise in their spectral background. The spectra of $\text{Nb}_2^+ - \text{Nb}_2$ and $\text{Nb}^+ - \text{Nb}_3$ cations did not exhibit any sharp rise in their spectral background. This is most likely due to the fact that the order of the resonance multiphoton process for these species does not change from an n -photon process to an $(n - 1)$ -photon process in the spectral region studied.

The orders of the resonance multiphoton process for the $^{90}\text{Zr}_2^+$ and Nb_2^+ cations, at the threshold energy, were determined from the fluence dependence study to be two- and three-photon processes, respectively, in agreement with density functional calculations (DFT) at the BLYP/Lan2dz level [33]. For the $\text{Nb}_3^+ - \text{Nb}$ cations, the previous collision-induced dissociation (CID) [27]

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measurements and density functional calculations [33] at the same level of theory suggest that the multiphoton process is a three-photon process for the $\text{Nb}_3^+ - \text{Nb}$ cation. Here, we measured the dissociation energies of these cations as $D_0(^{90}\text{Zr}_2^+) = 4.18 \pm 0.01$, $D_0(\text{Nb}_2^+) = 5.94 \pm 0.01$, and $D_0(\text{Nb}_3^+ - \text{Nb}) = 5.994 \pm 0.004$ eV. We also estimated the first ionization energy of $^{90}\text{Zr}_2^+$ to be 5.82 ± 0.01 eV using the thermochemical cycle. In addition, the dissociation energy of the Nb_2 was obtained as $D_0(\text{Nb}_2) = 5.43 \pm 0.01$ eV, using the thermochemical cycles.

2. Experimental procedure

A brief outline of the experimental procedure is given here, as detailed descriptions can be found elsewhere [32,33]. The apparatus used in the present study is specifically designed for the study of the photofragmentation of isolated, internally cold, chemically bonded cluster ions. It consists of a three-stage differentially evacuated chamber, which contains a laser vaporization cluster-ion source, a mass-selection section, which consists of a time-of-flight (TOF) mass spectrometer followed by a mass gate, and a tandem reflectron TOF mass spectrometer. The ion source has been developed for production of positively and negatively charged cluster species prior to supersonic expansion to minimize the internal excitation of the parent ions and, therefore, its effect on the photofragmentation process. A metal atom plasma is formed by pulsed laser vaporization of a metal target rod (Goodfellow, 99.9%) mounted in a cluster source fixture. The second harmonic output (532 nm) of an Nd:YAG laser is used for this purpose, focusing a 20–35-mJ, 10-ns pulse duration onto the rod source with a lens. Crucial to the successful generation of a fairly intense beam of niobium or zirconium cluster cation molecules was the continual ablation of the rod surface until the deeply penetrating layer of metal oxide had been largely removed. Vaporization was synchronized to the passage of the peak of a pulse of helium gas from a commercial molecular beam valve (120–140 psi backing pressure) over the target. The cluster concentration was augmented by allowing the gas mixture to pass through to the clustering channel, prior to supersonic expansion into vacuum and the first TOF stage. The selected niobium and zirconium cluster cations (Nb_n^+ and $^{90}\text{Zr}_2^+$) were thereafter fragmented by an Nd:YAG-pumped (532 nm), tunable-pulsed PDL dye laser in the 15,500–18,500 cm^{-1} region. A tandem TOF mass spectrometer and reflectron have been constructed to monitor the dissociation caused by pulsed laser fragmentation of the initially mass-selected cluster ions. This spectrometer is optimized to allow for maximum overlap of the ion and dissociation laser beams. In order to distinguish the parent and fragmented particles from each other, the reflectron acts as a second TOF spectrometer to separate the fragment and the parent in time. The resulting particles are then

detected by a microchannel plate (MCP). Spectra are obtained by monitoring the intensity of a chosen fragment ion as a function of photo-fragmentation wavelength.

3. Zirconium dimer cation ($^{90}\text{Zr}_2^+$)

3.1. Dissociation fluence dependence study

The background of the spectrum of Fig. 1 is due to multiphoton fragmentation dissociation of $^{90}\text{Zr}_2^+$ into the $^{90}\text{Zr}^+$ fragment. A sharp threshold may be seen at $16,870 \pm 40 \text{ cm}^{-1}$, and preliminary calculations indicate that this represents a change from a three-photon to a two-photon dissociation. In order to check this, we carry out fluence-dependent studies. Fig. 2 shows the fluence dependence for dissociation of $^{90}\text{Zr}_2^+$ into the Zr^+ fragment, both above and below the observed threshold. The pulsed photo-fragmentation dye laser beam is fixed at 16,795, 16,949, and 17,889 cm^{-1} , respectively. The intensity of the fragmented zirconium cation Zr^+ was then detected as a function of the fluence. The order of the absorption event leading to dissociation was found from the extent of the fragmentation as a function of laser fluence to be 2.29 at 16,795 cm^{-1} , 1.09 at 16,949 cm^{-1} , and 1.2 at 17,889 cm^{-1} . The dissociation fluence dependence of fragmentation of the Zr_2^+ does not give the exact order of the fluence-dependent fragmentation curves for the following reasons: (i) Ideally, either in the determination of the one-photon absorption cross-section or in the discrimination between one- and multiphoton processes, one would irradiate an ensemble of absorbers with a homogeneous light field of known absolute flux (photons $\text{cm}^{-2} \text{ s}^{-1}$) and determine the per-molecule

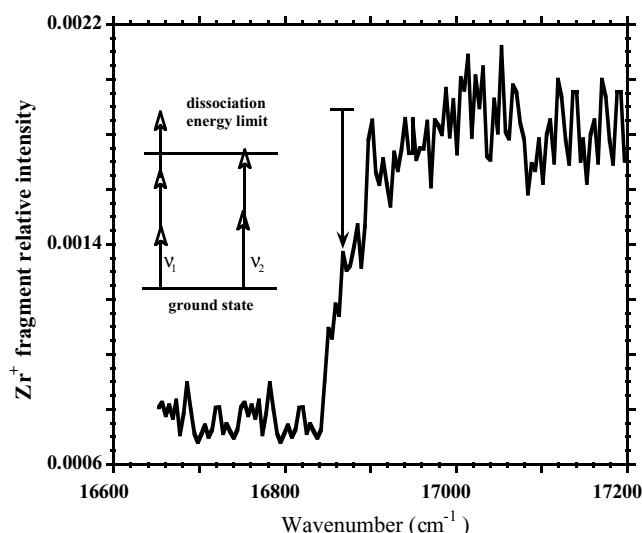


Fig. 1. The spectrum of the $^{90}\text{Zr}^+$ fragment ion exhibits a sharp rise above the background spectra at $16,870 \pm 40 \text{ cm}^{-1}$, as indicated by the arrow. The horizontal bar at the top of the arrow indicates the assigned uncertainty. The estimated fragmentation laser fluence was about $5 \pm 0.5 \text{ mJ cm}^{-2}$.

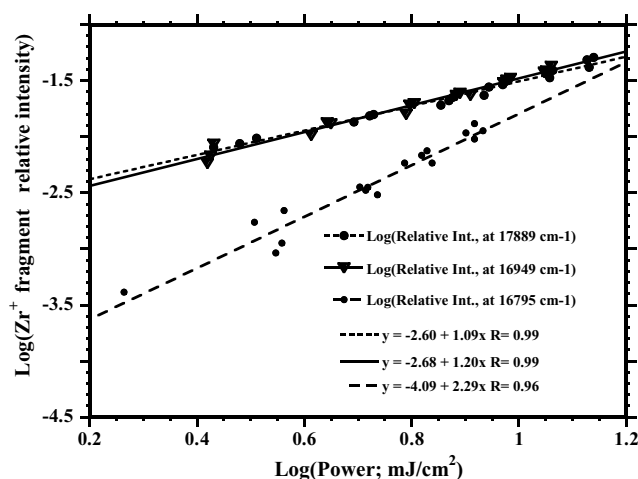


Fig. 2. The intensity of the fragment zirconium cation ($^{90}\text{Zr}^+$) detected as a function of the relative fluence. The order of the absorption event leading to dissociation was found from the extent of fragmentation as a function of laser fluence to be (a) 2.29 at $16,795\text{ cm}^{-1}$, (b) 1.09 at $16,949\text{ cm}^{-1}$, and (c) 1.20 at $17,889\text{ cm}^{-1}$.

absorption rate as a function of this intensity. This scenario is practically unrealizable, particularly when intrinsically pulsed experiments are performed. In the pulsed case, the incident light-field intensity varies in time from zero to some maximum value and back again, not necessarily monotonically (because of, for example, longitudinal cavity mode beating in a laser). The ideal experiment is then reduced to the measurement of the absorption of the molecular ensemble as a function of the pulse-integrated flux or fluence (photons cm^{-2} pulse). (ii) In averaging over the temporal profile of the light pulse, most experimental situations have imperfect overlap of the light field and the molecular ensemble producing sub-ensembles that receive different fluences, all contributing to the observed signal. This is typical for experiments with a pulsed laser, which exhibits high spatially structured output beams. Therefore, two-photon absorption events have a fluence dependence less than 2, three-photon events have a fluence dependence less than 3, etc. [34,35].

3.2. Multiphoton fragmentation of $^{90}\text{Zr}_2^+$

As mentioned in the previous section, Fig. 1 shows the one-color, two-photon fragmentation spectrum of $^{90}\text{Zr}_2^+$ into Zr^+ . In the range $16,100\text{--}18,400\text{ cm}^{-1}$, the spectrum of the Zr^+ fragment ion exhibits a sharp rise in the background at $16,870 \pm 40\text{ cm}^{-1}$. Evidence from the above studies of dissociation fluence dependence indicates that the multiphoton process is a three-photon process before the threshold and is a two-photon process after threshold ($16,870 \pm 40\text{ cm}^{-1}$). Thus, the dissociation energy of Zr_2^+ is determined to be $33,740 \pm 80\text{ cm}^{-1}$ (or $4.18 \pm 0.01\text{ eV}$). This value can be combined with the known ionization energy of Zr ($\text{IE} = 6.953\text{ eV}$ or $56,077\text{ cm}^{-1}$) [37] and dissociation energy of

Zr_2 ($D_0 = 3.052 \pm 0.01\text{ eV}$) [36] and using the thermochemical cycle

$$\text{IE}(\text{Zr}_2) = \text{IE}(\text{Zr}) + D_0(\text{Zr}_2) - D_0(\text{Zr}_2^+)$$

to obtain the ionization energy of Zr_2 as $\text{IE}(\text{Zr}_2) = 5.82 \pm 0.01\text{ eV}$ in agreement with the DFT prediction (at the BLYP/Lan12dz level), 5.703 eV the DFT for the ionization of Zr_2 ($^3\Delta_g$) to the $\text{Zr}_2^+(^2\Sigma_g^+)$ [33].

In the range $16,100\text{--}18,400\text{ cm}^{-1}$, three electronic transitions were observed. One of them was relatively weak at $17,880\text{ cm}^{-1}$ and the other two were at $18,290$ and $18,350\text{ cm}^{-1}$. Without high-resolution spectra, it is difficult to assign electronic transitions based in part on the only these three peaks. We could not examine structure farther to the blue due to lack of suitable optics to extend the dye laser range further.

4. Niobium dimer cation (Nb_2^+)

Fig. 3 shows the multiphoton, photo-fragmentation spectrum of Nb_2^+ into Nb^+ in the region $15,500\text{--}16,100\text{ cm}^{-1}$. The background of the spectrum exhibits a fairly sharp rise at the threshold, $15,975 \pm 25\text{ cm}^{-1}$. Fluence-dependent studies on Nb_2^+ at $17,857$ and $17,849\text{ cm}^{-1}$ were performed to determine the order of the multiphoton process in a manner similar to that of Zr_2^+ , discussed above. However, since the dye laser intensity drops considerably, we could only make good measurements on the high-energy side of the observed threshold. The order of the absorption event, leading to dissociation, was estimated from the fluence dependence of the intensity of Nb^+ fragments to be about 2.4 at $17,857$ and $17,849\text{ cm}^{-1}$, as shown in Fig. 4. As discussed above, because of fluctuations in the laser and cluster beams and mismatch in the laser and cluster ion beam overlap, the apparent order of a multiphoton process will be somewhat less than the actual order. From this, it appears that the fragmentation in this region must be a three-photon process. Additional information supporting this view comes from a previous determination by collision-induced dissociation of the bond dissociation energy of Nb_2^+ ($5.87 \pm 0.12\text{ eV}$) [27] and several DFT calculations [33]. The lowest dissociation threshold energy of Nb_2^+ is therefore $47,925 \pm 75\text{ cm}^{-1}$ ($5.94 \pm 0.01\text{ eV}$), in agreement with the collision-induced dissociation experiment. This value can be combined with the known ionization energy of Nb ($\text{IE} = 6.88\text{ eV}$) [38] and Nb_2 ($6.368 \pm 0.001\text{ eV}$) [12] to obtain the dissociation energy of Nb_2 to be $5.43 \pm 0.01\text{ eV}$, using the thermochemical cycle

$$\text{IE}(\text{Nb}_2) = \text{IE}(\text{Nb}) + D_0(\text{Nb}_2) - D_0(\text{Nb}_2^+).$$

In addition, we observed somewhat complicated electronic transitions in the multiphoton fragmentation spectrum of the Nb^{2+} cation in the $16,000\text{--}18,500\text{ cm}^{-1}$ region [33]. This result will be published elsewhere [32].

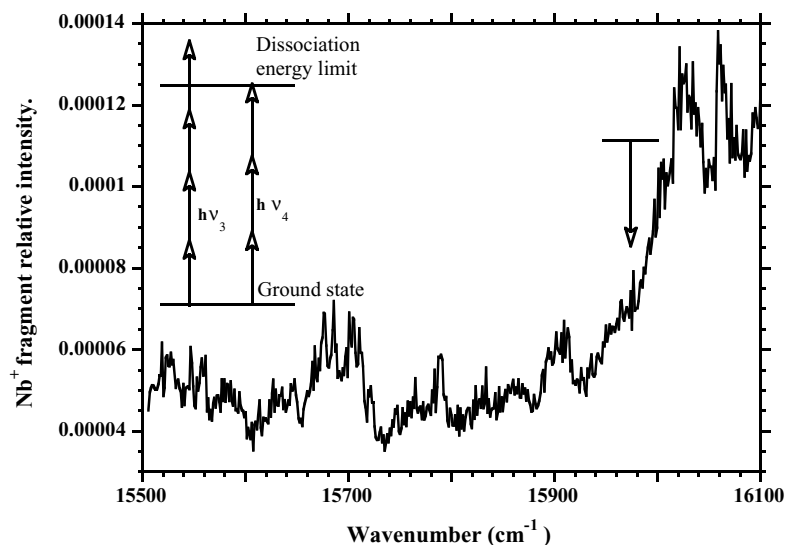
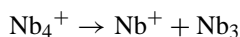
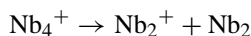


Fig. 3. The multiphoton photofragmentation spectrum of Nb_4^+ into Nb_3^+ in the region $15,500\text{--}16,100\text{ cm}^{-1}$. The background of the spectrum exhibits a fairly sharp rise at the threshold, $15,975 \pm 25\text{ cm}^{-1}$, as indicated by the arrow. The horizontal bar at the top of the arrow indicates the assigned uncertainty. The estimated fragmentation of laser fluence was about $6 \pm 0.5\text{ mJ cm}^{-2}$.

5. Niobium tetramer cation (Nb_4^+)

We now examine photofragmentation of Nb_4^+ into three possible fragmentation pathways in the ranges $16,060\text{--}16,380$, $16,800\text{--}17,100$, and $17,700\text{--}18,000\text{ cm}^{-1}$



No optical resonances were found in these regions. However, the multiphoton fragmentation spectrum of the Nb_3^+

fragment ion exhibited a sharp rise in the background at $16,115 \pm 10\text{ cm}^{-1}$ (Fig. 5). The dissociation energy of the $\text{Nb}_3^+\text{--Nb}$ has been found to be 6.00 ± 0.30 and $5.90 \pm 0.20\text{ eV}$ by Armentrout and co-workers [25,27]. These results suggest that the multiphoton process at the observed threshold ($16,115 \pm 10\text{ cm}^{-1}$) in the photofragmentation experiment is a three-photon process. The threshold energy of the $\text{Nb}_3^+\text{--Nb}$ fragment ion was then determined to be $5.994 \pm 0.004\text{ eV}$, in excellent agreement with both the previous experimental results [25,27]. A useful review of a considerable body of experimental data on dissociation energies has been written by Ervin [22].

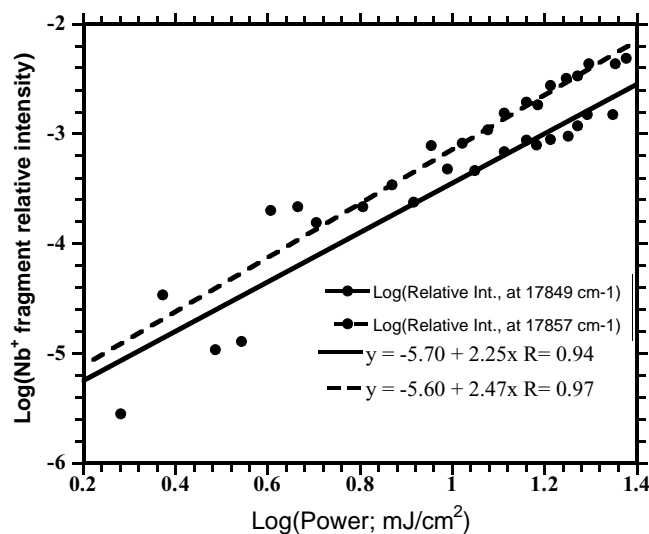


Fig. 4. Plot of Nb_3^+ fragment relative intensity vs. laser power for fluence dependence studies at $17,849$ and $17,857\text{ cm}^{-1}$.

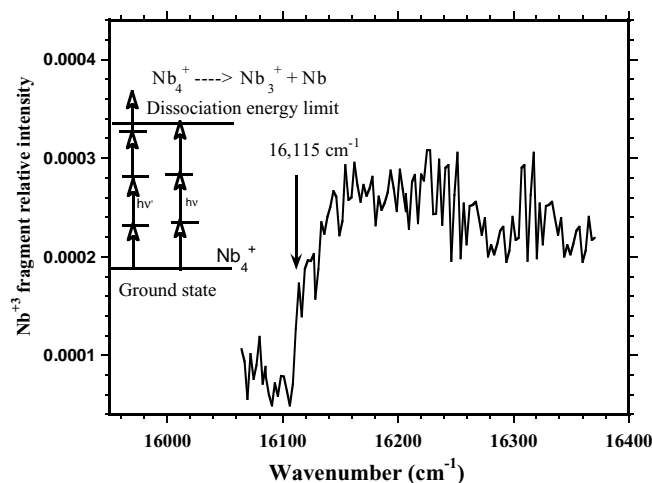


Fig. 5. The multiphoton fragmentation spectrum of $\text{Nb}_3^+\text{--Nb}$ exhibits a sharp rise at $16,115 \pm 10\text{ cm}^{-1}$. The estimated fragmentation laser fluence was about $5 \pm 0.5\text{ mJ cm}^{-2}$.

Table 1

Measured dissociation energies (in eV) of the zirconium dimer cation and niobium dimer, trimer, and tetramer cations

	Present work	CID
$D_0(\text{Zr}_2^+)$	4.18 ± 0.01^a	
$\text{IE}(\text{Zr}_2)$	5.82 ± 0.01^b	
$D_0(\text{Nb}_2^+)$	5.94 ± 0.01^a	5.87 ± 0.12^c
$D_0(\text{Nb}_2)$	5.43 ± 0.01^b	
$D_0(\text{Nb}_3^+ - \text{Nb})$	5.994 ± 0.004^a	6.00 ± 0.30^c 5.90 ± 0.20^c

^a Measured by resonance multiphoton photofragmentation techniques [27].

^b Estimated using thermochemical cycle, see text for detail [27].

^c Determined by collision induced dissociation (CID) experiments [27].

6. Conclusion

In conclusion, we have studied multiphoton fragmentation of zirconium dimer cation in the range $16,100\text{--}18,400\text{ cm}^{-1}$. Observation of the fragmentation spectrum spectrum of Zr^+ indicates a sharp threshold in the background at $16,870 \pm 40\text{ cm}^{-1}$. Studies of fluence dependence of the multiphoton process is a three-photon process below the threshold and is a two-photon process above the threshold. The dissociation energy of the $^{90}\text{Zr}_2^+$ is then measured, $D_0 = 4.18 \pm 0.01\text{ eV}$, for the first time. Furthermore, in the range $16,100\text{--}18,400\text{ cm}^{-1}$, three electronic transitions were observed. One of them at $17,880\text{ cm}^{-1}$ is relatively weak and the other two are seen at $18,290$ and $18,350\text{ cm}^{-1}$.

The multiphoton fragmentation of niobium dimer cation has been studied in the range $15,500\text{--}18,500\text{ cm}^{-1}$. The resonant multiphoton fragmentation spectrum shows a complicated pattern of electronic transitions in the $16,000\text{--}18,450\text{ cm}^{-1}$ region and exhibit a fairly sharp rise at $15,975 \pm 25\text{ cm}^{-1}$. The studies of dissociation fluence dependence and CID measurement, $D_0 = 5.87 \pm 0.12\text{ eV}$ [27], indicate that this sharp rise in the background is due to the change of multiphoton process from a four-photon process to a three-photon process. The measured dissociation energy of Nb_2^+ , $5.94 \pm 0.01\text{ eV}$, is in agreement with previous CID measurements.

The experimental results suggest that the multiphoton fragmentation in Nb_4^+ process should be a three-photon process at the dissociation threshold. The total energy of three photons gives a value of $5.994 \pm 0.004\text{ eV}$ for the fragmentation of initially mass-selected Nb_4^+ ion to the $\text{Nb}_3^+ + \text{Nb}$ -separated fragment limit. The measured dissociation energy of the zirconium dimer cation ($^{90}\text{Zr}_2^+$) was used in the thermochemical cycle equations with the known first atomic ionization energy and the known dissociation energy of neutral zirconium dimer, Zr_2 , to obtain the first ionization energy of Zr_2 . In addition, the measured value of $D_0(\text{Nb}_2^+)$ was combined with the values of $\text{IE}(\text{Nb})$ and $\text{IE}(\text{Nb}_2)$ to obtain a more precise value of the dissociation

energy of the neutral niobium dimer. These results are summarized in Table 1.

Acknowledgements

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