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# Photodissociation of $Kr_n^+$ clusters

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The photodissociation of  $Kr_n^+$  (3 < n < 11) cluster ions is observed for the first time in the 565 to 630 nm wavelength range.  $Kr_3^+$  has a photodissociation cross section of  $(8.1\pm0.8)\times10^{-17}$  cm<sup>2</sup> at 612 nm, while Kr<sub>4</sub><sup>+</sup> and Kr<sub>5</sub><sup>+</sup> are found to have larger photodissociation cross sections than  $Kr_3^+$  with a slightly red-shifted spectrum. Only  $Kr^+$  is detected as a photofragment of  $Kr_3^+$ , while in the  $Kr_n^+$  (4 $\leq n \leq 7$ ) experiments, both  $Kr_2^+$  and  $Kr^+$  photofragments are seen. As size *n* increases from 7 to 11,  $Kr^+$  disappears and  $Kr_3^+$  appears. Laser power studies show that all are single photon photodissociation processes. For higher order  $Kr_n^+$  clusters ( $4 \le n \le 7$ ) the intensity ratio between the two photodissociation products  $Kr_2^+$  and  $Kr^+$  is dependent on the wavelength of the laser light used in the photodissociation, but independent of the polarization direction of the laser. Translational energy analysis of the photofragments is used to investigate the photodissociation mechanisms. In contrast to the photodissociation of  $Kr_{2}^{+}$ , where two types of Kr<sup>+</sup> photofragments with different values of translational energy release are observed, only one type of  $Kr_2^+$  photofragment, with zero kinetic energy release is found in the  $Kr_4^+$  photodissociation. These findings are discussed in terms of the dynamics of photodissociation and possible structures of these cluster ions.

## **I. INTRODUCTION**

At the present time there is extensive interest in the properties, structure, and metastability of rare gas cluster ions. A subject of considerable attention centers on identifying the nature of the core ion with some studies pointing to the dimer ion and others to the trimer.<sup>1-7</sup> Investigations of photodissociation cross sections and dynamics of photodissociation are particularly pertinent in this regard. Herein, we present the results of recent investigations of the dynamics of dissociation of krypton cluster ions.

Krypton cluster ions are believed to be important intermediate species in a krypton-excimer laser process. Nighan *et al.*<sup>8</sup> have found that the four-atom rare gashalide exciplex  $Kr_3F$ , may have an important bearing on an Ar-Kr buffer mixture media in excimer lasers. And their experimental results showed that  $Rg_2X$  to  $Rg_3X$  reaction kinetics may play a significant role in determining the conditions typical of many rare gas-halide lasers.

Investigation of photodissociation of  $Kr_2^+$  can be traced back to the early work done by Miller et al.<sup>9</sup> and Lee et al.<sup>10</sup> where they measured the photodissociation cross section in the wavelength ranges 350 to 530 nm, 565 to 695 nm, and 620 to 860 nm. In the first range, the cross section decreases monotonically with increasing photon wavelength from 350 to 500 nm and has values of  $24.8 \times 10^{-18}$  $cm^2$  at about 356 nm. In the second range, the cross section increases when the photon energy increases. And in the last wavelength range, the cross sections have a broad maxima at 685 nm with a value of  $2.9 \times 10^{-18}$  cm<sup>2</sup>. In another experiment, Zamir et al.<sup>11</sup> studied rare gas excimer kinetics by using an electron beam to pump the rare gas krypton. Their experiments showed that the gas had an absorption cross section of  $\sigma = 3 \times 10^{-17}$  cm<sup>2</sup> at 502 nm which is larger than the value of  $Kr_2^+$  reported by Miller et al.

Michels *et al.*<sup>12</sup> suggested that this may be due to the presence of trimer noble-gas ions which would likely be present under the high-pressure condition of Zamir *et al.*'s experiments.

There have been some important theoretical investigations about structures and photodissociation properties of  $Rg_n^+$  clusters. For  $Rg_2^+$ , Wadt<sup>13</sup> has conducted *ab initio* polarization configuration interaction (POL-CI) calculations including spin-orbit coupling, to investigate the electronic states of  $Rg_2^+$ , and its absorption cross section. For  $Rg_3^+$ , Wadt<sup>14</sup> carried out *ab initio* polarization configuration interaction (POL-CI) calculations to deduce the geometry and spectral properties of rare gas trimer cluster ions. On this basis, all four rare-gas-trimer ions,  $Ne_3^+$ ,  $Ar_3^+$ ,  $Kr_3^+$ , and  $Xe_3^+$ , are found to have linear structures and all dipole allowed transitions are predicted to occur in the visible range.

The dissociation energy of  $Kr_3^+$  relative to  $Kr^+$  has been determined by Fehsenfeld *et al.*;<sup>15</sup> a value of 0.27 eV was deduced for  $Kr_3^+$  separating to  $Kr_2^+$  and Kr. The dissociation energy of the  $Kr_2^+$  ground state relative to  $Kr^+$  has been determined as 0.995–1.21 eV by photoionization,<sup>16–18</sup> rainbow scattering,<sup>19</sup> and photodissociation.<sup>20</sup>

Although there have been several photodissociation experiments done on  $Ar_n^+$ ,<sup>1-7</sup> there are none reported for  $Kr_n^+$  where n > 2. The availability of such data would enable a very interesting comparison between the  $Ar_n^+$  and the  $Kr_n^+$  systems. In the present work we present measurements on the photodissociation spectrum of  $Kr_3^+$ ,  $Kr_4^+$ , and  $Kr_5^+$  in the visible range, the results of a photodissociation product study of  $Kr_n^+$  ( $3 \le n \le 11$ ) and the results of the translational energy analysis in photodissociation processes of  $Kr_3^+$  and  $Kr_4^+$ .

## II. EXPERIMENTAL

A detailed description of the experimental setup has been given elsewhere.<sup>21-23</sup> Briefly, in the source chamber, about 1 atm of krypton gas is expanded through a 25  $\mu$ nozzle orifice which is surrounded by a thermostatically controlled cooling coil. Ionization of the neutral beam is effected by impact of a well collimated 100 eV energy electron beam. In the second chamber, a Wien filter is used to select the ion of interest, which is then focused into the laser interaction region. For most experiments, the Wien filter magnet is operated at a current of 2 A. In experiments requiring precise identification of product channels and branching ratios, the magnet current is raised to 5 A to increase the Wien filter resolution and prevent leakage of  $Kr^+$  through the Wien filter. In the photodissociation branching ratio experiments, the laser-ion beam interaction region is typically held at several volts attractive with respect to the birth potential of the ion. Following interaction of the ions with the laser light, the fragment ions and the remaining parents are accelerated into the quadrupole mass spectrometer. A mass programmer (Finnegan) enables up to eight mass windows of preset mass and width to be scanned. Through the external command electronics of the quadrupole control, the programmer sweeps the quadrople mass spectrometer across these windows. The width of the windows is set wide enough to cover the whole mass envelope due to different combinations of isotopes of Kr for a given size cluster. Hence, the intensities of the photofragments represent integrals across the whole mass envelope. In this way, isotope effects on branching ratio determination can be eliminated. The signals from these windows are then amplified and sent to and accumulated in a multichannel analyzer (MCA). The integrated intensity of each ion, with and without the laser, are then transferred to a computer. The importance of counting ions with and without the laser is that all signals taken into account are then exclusively from photodissociation and not influenced by other processes such as collision-induced dissociation.

In the experiments of the photofragment translational energy release, the interaction region is held at 100 V attractive with respect to the birth potential of the ion. The photofragment ions are passed through a three-grid retarding field type energy analyzer before entering the quadrupole, and a digital ramp generator is used to scan the potential on the central grid of the energy analyzer. The ramp generator is tied to the MCA such that the potential is changed when the MCA channel number changes. Thus, the same potential is applied to the grid every time the MCA is in a given channel. Only ions with energy greater than the potential on the central grid can pass through the analyzer, enter the quadrupole and be detected; all others are repelled. Experiments, therefore, generate the integral of the lab frame energy distribution of the ion. The actual energy distribution is obtained by numerically differentiating the raw data after using a least-squares polynomial smoothing routine.<sup>23</sup>

The resolution of the three-grid retarding-type energy analyzer is determined by Simpson<sup>24</sup> as  $\Delta E/E = \sin^2 \theta$ , where E is the energy of the charged particle and  $\theta$  is the angular spread seen by the analyzer. As mentioned in a previous paper,<sup>4</sup> the detector acceptance angle of the energy analyzer located 5 cm from the interaction region, is about 4° centered at  $\theta = 0$ . The resolution of the energy analyzer is  $\Delta E/E \approx 0.005$ . This resolution is completely adequate for distinguishing different photodissociation channels.

The argon ion laser beam is chopped to allow monitoring of fragment and parent intensities with and without the laser. The cavity of the dye laser has been extended to a length of 1 m, so that experiments can be carried out intracavity. The intracavity power of the dye laser cannot be monitored directly. Hence, in order to obtain these values, the light which is transmitted through the output coupler is collected by a power meter and a transmission function of the output coupler at wavelength  $\lambda$  (measured with a Hewlett Packard UV/VIS spectrophotometer) is employed to convert power meter readings to the dye laser intracavity power.

#### **III. RESULTS AND DISCUSSION**

#### A. Photodissociation

The absolute cross section of photodissociation is determined from the parent disappearance by using

$$p_{\rm on}/p_{\rm off} = \exp(-\sigma j_L d/v_p), \qquad (1)$$

where  $p_{on}$  and  $p_{off}$  are the parent ion intensities with and without the laser light, respectively,  $\sigma$  is the cross section, d is the diameter of the laser beam,  $v_p$  is the velocity of the parent ions in the interaction region (which can be determined by parent ion translational energy analysis), and  $j_L$  is the laser fluence. The laser power inside the dye laser cavity is carefully controlled so that only a one photon process can take place. (This point is further discussed in a later section.) Usually, only a few percent depletion rate of the parent ions is observed in the experiments. Using this procedure we obtained very good agreement with the values for  $Ar_3^+$  also investigated by the Lineberger group.<sup>2</sup>

Figure 1 shows the photodissociation spectrum of  $Kr_3^+$  in the wavelength range 630 to 565 nm (which corresponds to an energy of 1.97 to 2.20 eV). In the same figure, the photodissociation spectrum of  $Ar_3^+$  is shown for comparison between the two gases. The spectrum of  $Ar_3^+$  shown here is slightly flatter than the one we displayed in Fig. 1 of a previous paper.<sup>4</sup> The reason is that the shape of the photodissociation spectrum of rare gas cluster ions is very sensitive to the temperature of the cluster ions shown in the theoretical calculations<sup>12</sup> and as experiments.<sup>4</sup> In this context, the shape of the tail to the red side of the peak in the cross section depends on the conditions of cluster formation. The largest contribution to the error bars in the cross section is the counting statistical uncertainty which is given by Poisson statistics. The error bars presented here represent one standard deviation of statistical uncertainty. In contrast to the flat spectrum of  $Ar_3^+$  in the 630 to 565 nm range,  $Kr_3^+$  shows a small peak



FIG. 1. Absolute cross section of  $Kr_3^+$  photodissociation into  $Kr^+$  and 2Kr in the range 565–630 nm, based on parent disappearance. The spectrum of  $Ar_3^+$  also displayed as a comparison.

with width  $\approx 534$  cm<sup>-1</sup>, centered at 612 nm. Based on Eq. (1), the absolute cross section for photodissociation of  $Kr_3^+$  is determined to be  $(8.1\pm0.8)\times10^{-17}$  cm<sup>2</sup> at this wavelength. It is interesting that in this wavelength region Zamir *et al.*<sup>11</sup> saw a broadband photoabsorption in their electron-beam pumped rare gases visible absorption experiments.

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Photodissociation of the higher order clusters  $Kr_4^+$ and  $Kr_5^+$  are also observed in this wavelength range. The photodissociation spectra of  $Kr_4^+$  and  $Kr_5^+$  cluster ions are shown in Figs. 2 and 3, respectively. The spectrum of  $Kr_3^+$  is also displayed in both figures to serve as a reference. Although the value of the photodissociation cross section of higher order clusters,  $Kr_n^+$ , is slightly larger than that of  $Kr_3^+$  and the peak of the spectrum is slightly red shifted, such clusters have almost the same magnitude of photodissociation cross section as  $Kr_3^+$ . The shift of major magnitude occurs between the dimer and trimer. The photodissociation of  $Kr_2^+$  was also investigated in the



FIG. 2. Absolute cross section of  $Kr_4^+$  photodissociation into  $Kr^+$ ,  $Kr_2^+$ , and neutral photofragments. The spectrum of  $Kr_3^+$  displayed for comparison.



comparison.

FIG. 3. Absolute cross section of  $Kr_5^+$  photodissociation into  $Kr^+$ ,  $Kr_2^+$ , and neutral photofragments.

The spectrum of  $Kr_3^+$  is displayed for

present study, but within the limits of experimental error no photodissociation was found in this wavelength range.

#### **B. Dissociation channels**

There are no experimental or theoretical data on the bond energies of higher order  $Kr_n^+$  ions. However, Hiraoka *et al.*<sup>25</sup> measured rate constants for the clustering reaction of  $Ar_n^+$  in a high-pressure mass spectrometer, and deduced that  $Ar_{n-1}$ -Ar ( $4 \le n \le 11$ ) has binding energies of 71-64 meV which can serve as a reference for  $Kr_n^+$ . Energetically it is possible to dissociate from  $Kr_n^+$  to the  $Kr_2^+$  or  $Kr^+$  for the photon energies employed in the present study.

In the photodissociation of the  $Kr_3^+$  in the 565 to 630 nm range, as in the case of  $Ar_3^+$  photodissociation,<sup>4</sup> the only observable product is  $Rg^+$ , i.e.,

$$Kr_3^+ + h\nu \rightarrow Kr^+ + neutral products.$$
 (2)

For the photodissociation of the  $Kr_4^+$  cluster in the same wavelength range we observe both  $Kr_2^+$  and  $Kr^+$  as photofragments, but not  $Kr_3^+$ , i.e.,

$$Kr_4^+ + h\nu \rightarrow Kr_2^+ + 2 Kr$$
 (or neutral cluster), (3)

$$Kr_4^+ + h\nu \rightarrow Kr^+ + 3 Kr$$
 (or neutral cluster). (4)

In the case of higher order  $Kr_n^+$  (4 < n < 7) clusters, the observed photofragments are both  $Kr_2^+$  and  $Kr^+$ , but not  $Kr_m^+$  ( $m \ge 3$ ), that is,

$$Kr_n^+ + h\nu \rightarrow Kr_2^+$$
 or  $Kr^+ +$  neutral products  
(4 < n < 7).

However, for larger clusters sizes, namely  $(8 \le n \le 11)$ ,  $Kr_3^+$  starts to appear as photofragment and the  $Kr^+$  channel diminishes to less than the detectable limit:

$$\operatorname{Kr}_{n}^{+} + h\nu \rightarrow \operatorname{Kr}_{2}^{+} \text{ or } \operatorname{Kr}_{3}^{+} + \text{neutral products } (8 \leq n \leq 11).$$
  
(6)

The percentage of  $Kr^+$ ,  $Kr_2^+$ , and  $Kr_3^+$  in the total amount of photofragments vs cluster size *n* at a wavelength of 614 nm is plotted in Fig. 4. Careful calibration of the quadrupole mass discrimination allows, at least semiquantitatively, the branching ratio of the photodissociation products to be determined. This calibration procedure was described in Ref. 26. It is very evident that the percentage of the dimer or trimer is higher when the size of the parent gets larger. These experimental results are consistent with those of Lineberger *et al.*<sup>3</sup> who found, that for small clusters, the averge number of neutral photofragments ejected increases in proportion to the size of the initial cluster ion.

The electron excitation energy often relaxes faster into vibrational energy than into other channels. Vibrationally



FIG. 4. The percentage of  $Kr^+$ ,  $Kr_2^+$ , and  $Kr_3^+$  in the total amount of photofragments vs cluster size *n* at laser wavelength 614 nm.

(5)

hot cluster ions tend to be cooled either by sequential loss of monomer units or possibly by ejection of polyatomic cluster units. In order to distinguish mechanisms, an unambiguous mass analysis of neutral products needs to be performed immediately after photodissociation. In the experiments, analysis of the neutral product was not done, so no discrimination between the two possible mechanisms can be made. Therefore, although  $Kr_m^+$  was not observed  $(m \ge 3)$  from the photodissociation of  $Kr_n^+$   $(n \le 7)$ , it is possible that higher order  $Kr_m^+$  was produced in the photodissociation reaction followed by sequential evaporation of neutral unit(s):

$$\operatorname{Kr}_{n}^{+} + h\nu \to \operatorname{Kr}_{n}^{+} * \to \operatorname{Kr}_{n-1}^{+} \to \cdots \to \operatorname{Kr}_{2}^{+} \to \operatorname{Kr}^{+} \quad (7)$$

within the time period (several tenths of microsecond) in which the photofragments spend traveling from the interaction region to the detector. Hence, it is possible that the reason that  $Kr_m^+$  ( $m \ge 3$ ) are not seen as photofragments is that  $Kr_m^+$  ( $m \ge 3$ ) would be too hot to survive, and would evaporate neutral atoms in order to reach a more stable species like  $Kr_2^+$  or  $Kr^+$ . For example, if  $Kr_4^+$  has the most stable structure similar to what Kuntz *et al.* predict based on their diatomic-in-molecule (DIM) calculation for  $Ar_4^+$  and  $Xe_4^+$ ,<sup>27</sup> that is,

$$\begin{bmatrix} \mathbf{Kr} \cdots \mathbf{Kr} \cdot \mathbf{Kr} \cdots \mathbf{Kr} \end{bmatrix}^{+}$$
(8)

[where c > a > b; for Ar<sub>4</sub><sup>+</sup> c = 6.07, a = 5.07, b = 4.86; and for Xe<sub>4</sub><sup>+</sup> c = 7.20, a = 6.42, and b = 6.31 (all measurements in units of bohr)]; then we could imagine that photoinduced electronically excited Kr<sub>4</sub><sup>+</sup> might dissociate its two wing neutral atoms and leave a vibrationally hot dimer which might or might not continuously evaporate to the final product Kr<sup>+</sup>.

One of our important findings for  $Kr_4^+$ ,  $Kr_5^+$ , and  $Kr_6^+$  shown in Figs. 5(a), 5(b), and 5(c), respectively, is that as the wavelength of the laser photon increases from 564 to 634 nm, the percentage of  $Kr_2^+$  in the photofragment dissociated from  $Kr_n^+$  (4 $\leq n \leq 7$ ) also increases. Interestingly, the  $Kr_2^+$  percentage increase is independent of cluster size. This finding shows that when the energy of the photon decreases, the photodissociation reaction is much more favorable to the less demanding energy channel, that is dissociation to  $Kr_2^+$ . And when the energy of the photon is larger; there are higher populations of  $Kr_2^+$  in vibrationally excited states which then exceed the dissociation limit and breaks into Kr<sup>+</sup> and neutral product. Since experiments have been done intracavity with respect to the laser, it is very easy to obtain greater than a 10% depletion. But, we have been careful to ensure that both  $Kr_2^+$  and  $Kr^+$ arise from one-photon dissociation processes as established via power studies for both photofragments shown in Fig. 6. The data are consistent with a line of slope = 1, which is expected for a one-photon process.

Another interesting finding is that there are no significant changes in the ratios of the photofragments, nor in their dependence on laser wavelength, when the polarization direction of the laser is tuned parallel to the ion beam instead of perpendicular as used in all data collection for the results discussed above. The experimental results imply



FIG. 5. The percentage of  $Kr^+$  and  $Kr_2^+$  photodissociated from  $Kr_n^+$  vs laser wavelength. (a)  $Kr_4^+$ , (b)  $Kr_5^+$ , (c)  $Kr_6^+$ .



FIG. 6. Power study for both Kr  $^+$  and Kr  $_2^+$  photofragments dissociated from Kr  $_4^+$ .

that  $Kr_2^+$  and  $Kr^+$  dissociate from the same energy surface, but from different sequential dissociation steps. In a previous paper,<sup>4</sup> a sequential dissociation mechanism was used to describe this type of dissociation process.

#### C. Photofragment translational energy analysis

There have been some theoretical investigations about the structure of  $Rg_n^+$  clusters.<sup>12,27,28</sup> The ground state geometry of  $Rg_3^+$  is controversial. Based on translational energy analysis studies, our results show that it is possible to interpret the photodissociation dynamics data assuming  $Kr_3^+$  has a linear structure in its ground state as has been also indicated for  $Ar_3^+$ .<sup>4</sup>

The photodissociation process can take place by the following mechanisms:

$$\mathbf{Kr}_{3}^{+} \rightarrow [\mathbf{Kr}\cdots\mathbf{Kr}^{+}\cdots\mathbf{Kr}]^{*} \rightarrow \mathbf{Kr}^{+} + 2\mathbf{Kr}, \qquad (9a)$$

$$Kr_3^+$$
→ $[Kr^+ \cdots Kr \cdots Kr]^*$ → $Kr^+ + 2 Kr$  (or  $Kr_2^*$ ),  
(9b)

$$Kr_{3}^{HV} \rightarrow [(Kr-Kr)^{+} \cdots Kr]^{*}$$
$$\rightarrow (Kr-Kr)^{+*} + Kr \rightarrow 2 Kr + Kr^{+}. \qquad (9c)$$

If the lifetime of the transition states in reactions (9a), (9b), and (9c) are shorter than their rotational periods, the photofragment, in this case  $Kr^+$ , will carry different translational energy which is converted from excess electronic excitation energy in the photodissociation reaction. Even in this situation, mechanism (9a),  $Kr^+$  will carry zero translational energy release from the photodissociation; but in mechanisms (9b) and (9c) it will carry some amount of translational energy. In the case of mechanism (9c), the subsequent step leading to the dissociation of  $(Kr-Kr)^{+*}$  may lead to differences in the energy release into  $Kr^+$ , depending on the lifetime of  $[Kr-Kr]^{+*}$ . Additionally, it is possible for a zero kinetic energy release peak to show up in mechanism (9c) if dissociation occurs via a predissociating state as suggested for the case of  $Ar_3^+$ .<sup>4</sup> The translational energy analysis and release can be calculated using the method described in a previous paper.<sup>4</sup> The considerations which are important for the results presented herein are briefly described for the convenience of discussion.

The photofragment with translational energy,  $E_t$ , released in photodissociation appears in the lab frame with energy  $qU_f$ ,

$$U_{f}(0) = U_{b} - (1 - m_{1}/M)(E_{b}/q) \quad (E_{t}=0), \quad (10a)$$

$$U_{f}(E_{t}) = U_{f}(0) + \frac{1}{qM}(\cos^{2}\theta)m_{2}E_{t} + \frac{1}{q}\cos\theta(4m_{1}m_{2}E_{t}E_{b}/M^{2})^{1/2} \quad (E_{t}\neq0).$$
(10b)

Here, q is the charge of the particle,  $U_f$  is the potential at which the fragment is retarded by the voltage scanned grid energy analyzer,  $U_b$  is the birth potential of the parent ion which can be determined experimentally from energy analysis of the parent ion (all the potentials measured here are relative to ground state potential),  $\theta$  is the angle between the detectable fragment in the center-of-mass frame and the beam axis, and  $m_1$ ,  $m_2$ , and M are the masses of the charged fragment, neutral fragment, and parent, respectively. For the situation of photofragments scattered forward and backward with respect to the detector (i.e.,  $\theta = 0^\circ$ , 180°), the energy analyzer measures the photofragment energy along the beam axis.

Figure 7 shows the results of the translational energy analysis of  $Kr_3^+$  photodissociation at different laser wavelengths. There are two types of photofragments revealed by their distribution probabilities along the lab energy frame. According to Eqs. (10a) and (10b), the center peak arises from zero translational energy which suggests that the products giving rise to this peak come from mechanism (9a) [or possibly via a predissociating (9c) as mentioned above]. The two side peaks come from the photofragments having nonzero translational energies indicated in mechanism (9b) and/or (9c). In Fig. 7, the right side peak is the photofragment with  $\theta = 0^{\circ}$  (traveling toward to the detector), while the left side peak is due to the photofragment having  $\theta = 180^{\circ}$  (moving away from the detector). Thus by substituting  $\theta = 0^{\circ}$  and  $\theta = 180^{\circ}$  into Eq. (10b),  $q\Delta U_{f}$ , the width of the laboratory frame energy distribution spectrum is found as a function of  $E_p$  and is given by the following:

$$q\Delta U_f(E_t) = \left(\frac{4}{M}\right) (E_b E_t m_1 m_2)^{1/2}.$$
 (11)

Here,  $E_i$  can be related to the energy of the absorbed photon, hv, as

$$E_t = hv - D_0 + E_{int}^p - E_{int}^f.$$
 (12)

In the above equation,  $D_0$  is the dissociation energy of the ground state of the parent to the ground state of the fragments;  $E_{int}^p$  and  $E_{int}^f$  are the internal energies of the parent



FIG. 7. Translational energy analysis of  $Kr_3^+$  photodissociation at different laser wavelengths. The central peak arises from zero translational energy [mechanism (9a)]; the two side peaks come from photofragments having nonzero translational energies [mechanisms (9b) and (9c)].

and fragment, respectively. The  $E_{int}^{\rho}$  is considered negligible because the internal temperature of the ion cluster is expected to be very low due to the cooling effect arising from the supersonic expansion beam method used in the production of parent ions.<sup>4</sup>  $E_{int}^{f}$  is obviously very small because when Kr<sup>+</sup> is the photofragment, and the  $D_0$  for Kr<sub>2</sub> neutral is less than 0.02 eV,<sup>29</sup> very little internal energy can be stored in the neutral dimer. Now, Eq. (11) can be rewritten as

$$q\Delta U_f(h\nu) = \left(\frac{4}{M}\right) (E_b m_1 m_2)^{1/2} [2/3(h\nu - D_0)]^{1/2}.$$
(13)

A factor of 2/3 should be incorporated into the equation. This arises because detectable photofragment Kr<sup>+</sup> has 1/3 the mass of its parent Kr<sub>3</sub><sup>+</sup>, and it will carry two-thirds of the translation energy released from photodissociation according to the energy and momentum conservation laws.

Based on the foregoing considerations, experimentally increasing the photon energy will cause the two side peaks to move apart. In Fig. 8, the experimentally determined  $\Delta U_f$  data points are plotted with different photon energies, and a calculated curve drawn from Eq. (13) is shown for comparison. The calculated curve is obtained by using



FIG. 8. Experimental data,  $\Box$ , plot  $\Delta U_f$  with different photon energies. Solid line shows the theoretical predictions based on Eq. (13).

 $D_0 = 1.48$  eV taken from Ref. 15 and 19, and a value of  $E_b = 85.0$  eV determined from the parent beam energy analysis. Note there is a reasonably close match between experimental data points and the theoretical curve, indicating that the mechanism proposed here for the photodissociation of  $Kr_3^+$  is reasonable.

The experimental results shown in Fig. 7 were taken with a laser polarization angle of 54.7° with respect to the ion beam axis. Theoretically, in the recoil angle probability equation

$$P(\theta) = (\frac{1}{2}\sin\theta) [1 - \beta P_2(\cos\theta) P_2(\cos\phi)]$$
(14)

the second degree Legendre polynomial  $P_2(\cos \phi)$  goes to zero at this angle. Here,  $\phi$  is the laser polarization angle with respect to the ion beam axis,  $\theta$  has the same meaning as in Eq. (10b), and  $\beta$  is the asymmetry parameter which contains information on the excited state lifetime and transition symmetry. The measured distribution at this magic angle of 54.7° ideally will mimic the isotropic distribution,<sup>30</sup> so that the values of  $q\Delta U_f$  can be acquired more accurately. The asymmetric shape of the two wing peaks is a good indication that not all fragments ions are collected, and therefore we do not attempt to derive an asymmetry parameter  $\beta$ .

From the experimental results shown in Fig. 7, it is clear that when the photon energy is high enough (as it is at 545 nm), all three mechanisms are about equally probable. Thus, photofragments which dissociate through mechanism (9a) and show up as the central peak have the same probability of occurring as do those which dissociate by mechanisms (9b), and (9c), which show up as the side-wing peaks. But when the energy of the laser photon is lowered, the energetically favored mechanisms will be (9b) and (9c) because in (9b) and (9c) the cleavages of two chemical bonds in  $Kr_3^+$  happen sequentially instead of simultaneously such as in the case of mechanism (9a), so the central peak gradually vanishes. Hence, in this case a smaller fraction of the cluster ions dissociate to the zero



FIG. 9. The translational energy distribution of  $Kr_2^+$  from photodissociation of  $Kr_4^+$ , -50.5 eV in the lab energy frame is the zero point of the central mass frame energy. The data shows only one type of  $Kr_2^+$  photofragment with zero translational energy release. The data was collected at laser wavelength 614 nm and with the polarization of 0° with respect to the direction of the ion beam.

kinetic energy release  $Kr^+$  channel which is the one responsible for the central peak. This disappearance is in accord with what is actually observed in higher order  $Kr_n^+$  cluster dissociation experiments. In these experiments, the smaller the photon energy used, the higher the  $Kr_2^+$  ratio [see Figs. 5(a), 5(b), and 5(c) and discussion in Sec. III B].

One of the interesting findings in the translational energy analysis experiments of  $Kr_n^+$  is that when  $Kr_4^+$  dissociates, the only dimer product observed is the photofragment with zero translational energy. Figure 9 shows this result. When the parent beam energy is 100 eV, and the birth potential is 0.5 eV,  $U_f(0)$  predicted by Eq. (10a) will be equal to -50.5 eV which is exactly what is observed in Fig. 9. This could be explained if  $Kr_4^+$  ions have a linear structure and photodissociation of  $Kr_4^+$  to  $Kr_2^+$  can be described as the following:

$$[\mathbf{K}\mathbf{r}\cdots\mathbf{K}\mathbf{r}\cdots\mathbf{K}\mathbf{r}]^{+} + h\nu \rightarrow [\mathbf{K}\mathbf{r}\leftarrow(\mathbf{K}\mathbf{r}\cdots\mathbf{K}\mathbf{r})^{+}\rightarrow\mathbf{K}\mathbf{r}]$$
$$\rightarrow \mathbf{K}\mathbf{r} + \mathbf{K}\mathbf{r}_{2}^{+} + \mathbf{K}\mathbf{r}.$$
(15)

The neutral Kr atoms carry away all translational energy release from photodissociation so that  $Kr_2^+$  photofragments are observed with zero kinetic energy. Recently, Kuntz et al.<sup>27</sup> applied the diatomics-in-molecules (DIM) model to calculate the energy surfaces of homogeneous noble gas ions  $Ar_n^+$  and  $Xe_n^+$  (for n = 3, 4, ..., 22) with different possible structures. The results showed that for  $Rg_4^+$  ions, the most stable structure is linear, and consists of a distorted trimer with a nearly neutral atom appended [see Eq. (8)] which will support our proposed mechanism. Of course, this is not an exclusive explanation because if  $Kr_4^+$  photodissociation follows a sequential dissociation mechanism, then the intermediate state in the photodissociation process may experience several molecular rotations before it evolves to  $Kr_2^+$ . In this case, the structure of the parent ion Kr<sub>4</sub><sup>+</sup> could not be probed by translational energy release analysis. Obviously, more experimental evidence and theoretical work need to be done before confirming the structure of  $Kr_4^+$ .

### **IV. CONCLUSIONS**

(1) The photodissocation of  $Kr_n^+$  ( $3 \le n \le 11$ ) cluster ions are observed in the 565 to 630 nm wavelength range.  $Kr_3^+$  has a photodissociation cross section of ( $8.1 \pm 0.8$ )  $\times 10^{-17}$  cm<sup>2</sup> at 612 nm while  $Kr_4^+$  and  $Kr_5^+$  are found to have larger cross sections with a slightly red shifted spectrum.

(2) In the above wavelength range, the following dissociation channels are observed:

(A)  $\operatorname{Kr}_{3}^{+} + h\nu \rightarrow \operatorname{Kr}^{+} + \text{neutral product,}$ (B)  $\operatorname{Kr}_{n}^{+} + h\nu \rightarrow \operatorname{Kr}^{+} \text{ or } \operatorname{Kr}_{2}^{+} + \text{neutral product}$ 

(B)  $\operatorname{Kr}_{n}^{+} + h\nu \rightarrow \operatorname{Kr}^{+}$  or  $\operatorname{Kr}_{2}^{+}$  + neutral product (4 $\leq n \leq 7$ ), (C)  $\operatorname{Kr}_{n}^{+} + h\nu \rightarrow \operatorname{Kr}_{2}^{+}$  or  $\operatorname{Kr}_{3}^{+}$  + neutral product

(C)  $\mathbf{KI}_n^* + nv \rightarrow \mathbf{KI}_2^*$  of  $\mathbf{KI}_3^* + \text{neutral product}$ ( $8 \le n \le 11$ ).

(3) In the above equations (B) and (C), the product ratios of photodissociation are laser wavelength dependent, but not laser polarization direction dependent. In reaction (B), when the photon energy decreases, the dissociation reaction is more favorable to the  $Kr_2^+$  product channel. The photodissociation of  $Kr_n^+$  could either lose Kr fragments simultaneously [as in  $Kr_3^+$  mechanisms (9a) and (9b)] or lose Kr sequentially [as in  $Kr_3^+$  mechanism (9c)].

(4) The translational energy studies for  $Kr_3^+$  show that there are two types of  $Kr^+$  photofragments. The one with zero translational energy release can be described by the mechanism proposed in mechanism (9a), and the other can be described by the mechanisms proposed in (9b) or (9c). In the latter case, an increase in the photon energy will cause the translational energy of the photofragment to increase quadratically as predicted by Eq. (13).

(5). In the translational energy analysis of the  $Kr_2^+$  photofragment from dissociated  $Kr_4^+$ , the only type of  $Kr_2^+$  is the one with zero translational energy release. The experimental results are consistent with  $Kr_4^+$  having a linear structure.

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