Observation of linear isomers of the ionized rare gas tetramers Ar$_4^+$ and Xe$_4^+$

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The ionized rare gas clusters Ar$_4^+$ and Xe$_4^+$ have been studied by photofragmentation. Center-of-mass velocities of the neutral and ionized photofragments have been measured for photon energies between 1.6 and 4.4 eV. In almost all of the examined photon energy region, both clusters exhibit fragment velocity distributions which show that they consist of a linear ionized trimer with an additional atom loosely attached to its side. For the lowest photon energies, however, fragmentation patterns are observed which can only be explained by a linear tetramer structure. This demonstrates that stable linear isomers of the ionized rare gas tetramers exist. © *1999 American Institute of Physics.* [S0021-9606(99)00230-5]

I. INTRODUCTION

Rare gas clusters are simple systems, which nevertheless exhibit a wealth of interesting properties. Apart from helium clusters, the neutral rare gas clusters can be seen as assemblies of hard spheres interacting by van der Waals forces. This changes dramatically upon ionization of the cluster. One effect is a compression of the whole cluster due to the polarization interaction of the neutral atoms with the charge. Much more important, however, is the fact that the newly formed ion can form a strongly bound dimer with another atom. So a short time after ionization an ionized dimer core will be formed within the cluster, having a bond length much shorter than the neutral–neutral distance. This mechanism was recognized[1] shortly after first observations of ionized rare gas clusters in mass spectroscopical investigations. The question arises whether this ''charge delocalization'' will stop after formation of a dimer, or whether larger ionized core molecules will be formed. Theoretical investigations of argon and xenon clusters have predicted the formation of charged linear trimer or even tetramer cores.[2,3] Linear core molecules are generally preferred as the bonding is based on valence *p*-orbital overlap. Additionally in the case of the trimers there is a Jahn–Teller instability of the equilateral triangle structure, so that even He$_3^+$ is linear.

The existence of linear trimer molecules was unambiguously demonstrated by spectroscopical investigations of size selected ionized rare gas clusters. From helium to xenon the ionized trimer Rg$_3^+$ exhibits an absorption spectrum different from that of the dimer Rg$_2^+$.[4–9] Both exhibit one dominant broad absorption peak; for the trimers, however, it is always located at roughly half the energy than for the dimers. As this can be explained by simple considerations about the electronic states of the linear dimer and trimer molecules,[10] the existence of an at least almost symmetrical linear trimer can be seen as proven. For bigger clusters the absorption spectrum always is very similar to that of the trimer. With increasing size only a gradual shift of the absorption position to smaller photon energies can be observed, and in the case of xenon, a gradual splitting of the main trimer absorption

peak into two peaks.[5–7,9] From these findings it was concluded that the ionized linear trimer is the core molecule of the clusters, and that the shift of the absorption peaks is due to solvation effects, and to mixing of the excited core state with solvation shell charge transfer states.[3] Nevertheless there was also speculation whether the changes in the absorption spectra might be due to the development of a linear tetramer core. This open question was one of the reasons for the investigation presented here.

II. EXPERIMENT

The apparatus used in this experiment has been described in detail in a recent report.[11] Briefly, rare gas clusters are produced in a supersonic expansion, ionized by electron impact and mass selected in a reflectron-type time-of-flight mass spectrometer (TOF-MS). Packets of clusters of a chosen size are injected into a second linear TOF-MS, where they are accelerated and subsequently dissociated by a pulsed polarized laser beam. After passing another acceleration field and a field-free drift region of 0.5 m length the photofragments hit a microchannelplate detector. From the measured arrival time distributions one can determine the center-of-mass velocity distributions of the fragments. The weak acceleration field applied behind the laser interaction region serves to separate charged fragments of different masses. It should be emphasized that not only charged, but also neutral fragments are detected, as they are fragments of clusters with kinetic energies of a few thousand eV, and thus have sufficient kinetic energy to produce a signal on the microchannelplate.

The measured TOF spectra have been fitted with model functions, which have been calculated by transforming center-of-mass velocity and angular distributions into arrival time distributions.[11] As will be described in the next section, all photofragments of the ionized rare gas clusters have a bimodal velocity distribution: in the course of the fragmentation they either gain only a low center-of-mass velocity or are ejected with a rather high velocity. For these two types of fragments two different angular and velocity distributions
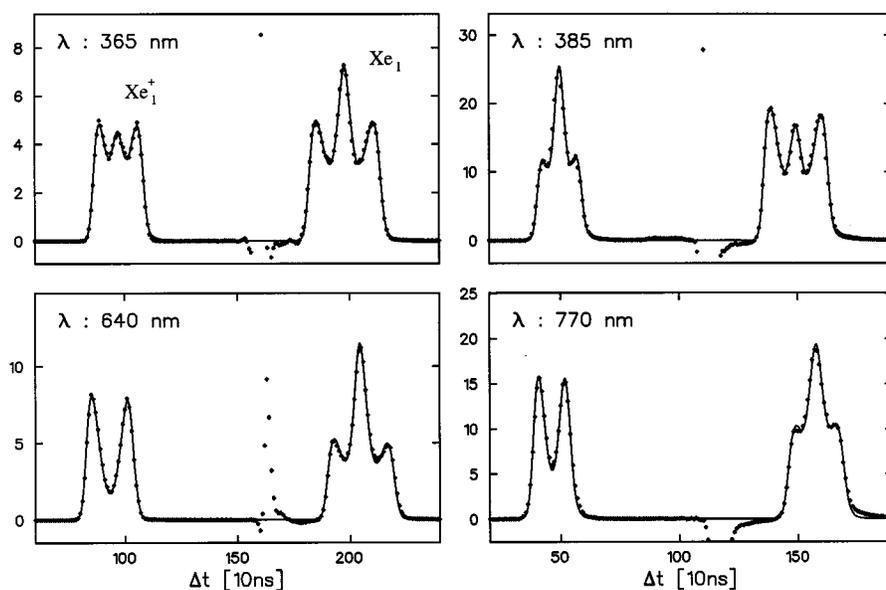
FIG. 1. Fragment TOF spectra of Xe_3^+ for different wavelengths, laser polarization parallel to the beam. From left to right first the fragments Xe_1^+, then neutral Xe_1 appear. The peak of the unfragmented Xe_3^+ is suppressed.

were used. For the slow fragments an angularly isotropic Boltzman-type velocity distribution was used, as one would expect for the emission of particles in thermal equilibrium:

$$f(v)dv = \frac{2}{\alpha^2} v \exp\left(-\frac{v^2}{\alpha^2}\right) dv.$$

For the fast fragments best fits were obtained with a $\cos^2$ angular distribution with respect to the laser polarization and a Gaussian velocity distribution:

$$f(v)dv = \frac{1}{\sigma\sqrt{\pi}} \exp\left(-\frac{(v-\bar{v})^2}{\sigma^2}\right) dv.$$

It should be noted that the examined clusters have a broad distribution of internal energies. As mentioned above, rare gas clusters are highly excited after ionization. They always evaporate several atoms until they reach an internal energy at which the evaporation rate is small enough so that they can survive within the experimental time window (about 100 μs). The internal energy distribution of the examined clusters will thus stretch from almost zero to a few times of the dissociation energy.

III. RESULTS

Before presenting the results obtained for the rare gas tetramers, we will briefly discuss the findings in the case of the trimer Xe_3^+, as the comparison of the trimer and tetramer results will be the essential part of our argument. Example arrival time spectra measured for Xe_3^+ at different photon energies are shown in Fig. 1. The polarization of the laser beam was parallel to the cluster beam direction, as it was in all measurements presented in this report.

In the spectra from left to right first the ionized monomers and then the neutral monomer photofragments appear. The peak of the unfragmented trimers has been suppressed by subtracting a scaled spectrum measured without laser ex-

citation, so that only a noisy negative peak can be seen at its position. No ionized dimer fragments have been observed in the examined photon energy range.

All of the trimer TOF spectra show a similar pattern. Both the peaks of the ionized and neutral monomer fragments are split into one central peak, indicating fragments which have not gained much velocity in the course of the dissociation, and two wings indicating fragments which have been ejected with high velocities (between 850 and 520 m/s) into and against the direction of the cluster beam. The separation between the wings is a measure for the kinetic energies of the fragments. This energy depends on the photon energy, the total cluster binding energy, and the final fine structure state of the ion, as has been discussed in detail in Ref. 11. The most interesting feature in these spectra is the ratio of the intensities of fast (wing peaks) and slow (central peaks) fragments. At 365 nm only a small amount of slow ions can be observed, while at 385 nm the slow ions prevail. At the two other wavelengths no slow ions at all can be observed. This is an important finding, and will be discussed later on.

In Fig. 2 arrival time spectra of Xe_4^+ are shown. These spectra are very similar to those of Xe_3^+ except for two differences. One difference is that for the two highest and for the lower photon energies ionized dimer fragments can be observed. At 365 nm and at 385 nm the peak of these dimer fragments is quite narrow, indicating low center-of-mass velocities ($\alpha = 110$ m/s). At 715 to 770 nm, however, the dimer peak is much broader. At 770 nm, e.g., the dimers have mean velocities of $\bar{v} = 345$ m/s ($\sigma = 120$ m/s). Here the intensity of the dimer peak is about three times as high as that of the ionized monomers.

The second difference between the tetramer and the trimer fragment arrival time spectra is the change of the form of the neutral monomer peak at the lowest photon energy. While at 770 nm the neutral monomer fragments of the trimer still exhibit the same three peak structures as observed
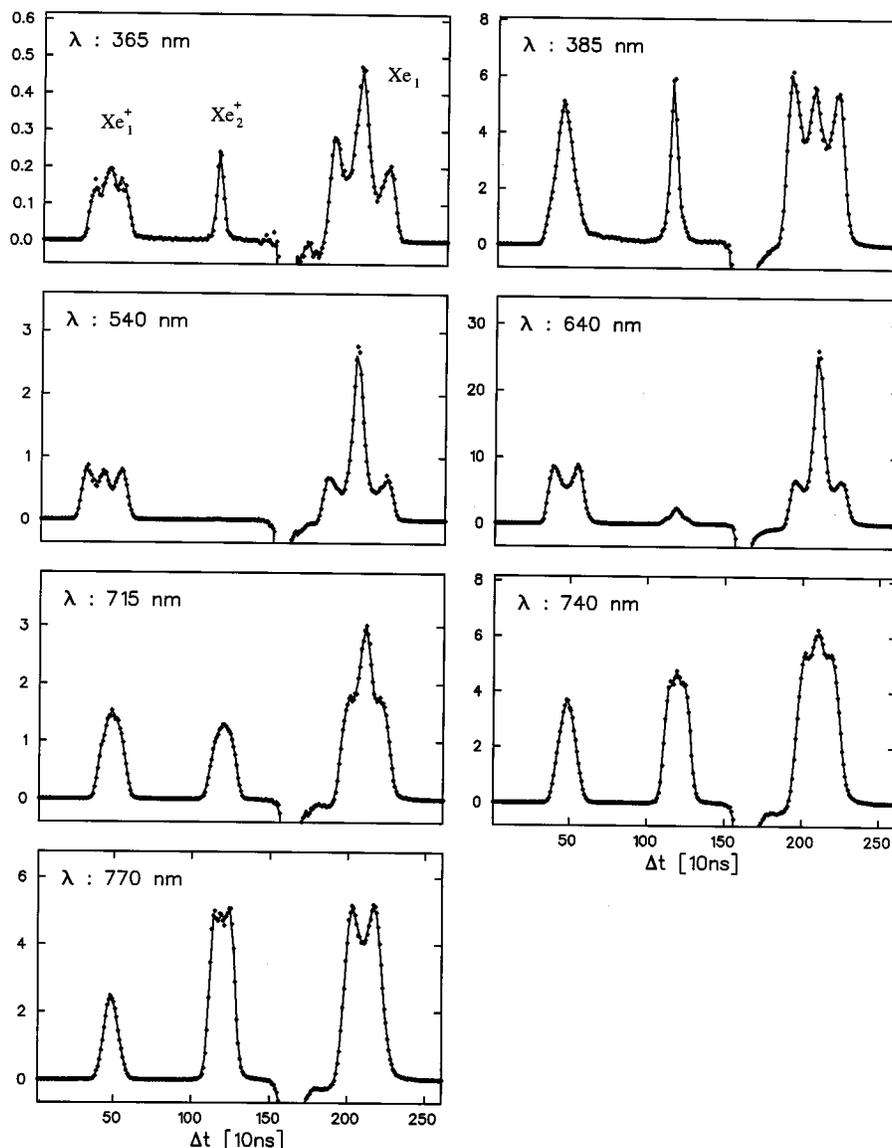
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FIG. 2. Fragment TOF spectra of Xe_4^+ for different wavelengths, laser polarization parallel to the beam. The appearing fragments from left to right are Xe_1^+, Xe_2^+, and neutral Xe_1. The peak of the unfragmented Xe_4^+ is suppressed.

for the shorter wavelengths, the neutral fragments of the tetramer only show two wings of fast particles. The respective mean velocity ($\bar{v} = 425$ m/s, $\sigma = 170$ m/s) is much lower than that measured for the fast fragments of the trimer ($\bar{v} = 570$ m/s), but is comparable to that of the ionized dimer fragments.

Conservation of momentum requires that if the tetramer broke up into a fast ionized dimer fragment and just one fast neutral fragment, the latter should have twice the velocity of the dimer. The observed velocities indicate, however, that the tetramer has broken up into two halves, that is an ionized dimer must have been ejected into one direction, and two neutral atoms into the other. These two fast neutral atoms seem to have some relative velocity, leading to the appearance of neutral atoms with slightly higher velocity than that of the dimers. An explanation for this peculiar fragmentation behavior will be given in the discussion.

One striking similarity between the TOF spectra of Xe_3^+ and Xe_4^+ can be seen in the behavior of the slow ion to fast ion intensity ratio. As observed for Xe_3^+, also in the case of

the tetramer the relative slow ion intensity is small at 365 nm, much higher at 385 nm, and small again for lower photon energies. As will be explained in the following section, this finding proves that an ionized xenon tetramer usually consists of an ionized linear trimer with a fourth atom loosely attached.

In Fig. 3 finally the results for the photofragmentation of Ar_4^+ are shown. As in the case of Xe_4^+, the ionized and neutral monomer fragments for wavelengths below 600 nm show the central peak plus wings structure, and again with a strongly changing relative intensity of the slow ions. Also ionized dimer fragments can be observed, the intensity of which strongly increases with photon wavelength. Again at the higher photon energies only slow dimers can be observed, while at the lowest energies fast ones prevail. At 680 nm for the neutral fragments almost only fast particles can be observed, the velocity of which ($\bar{v} = 740$ m/s) again corresponds to that of the dimer ($\bar{v} = 700$ m/s). One feature can be seen in these TOF spectra, which was not observed in the case of Xe_4^+. This is the appearance of very fast neutral
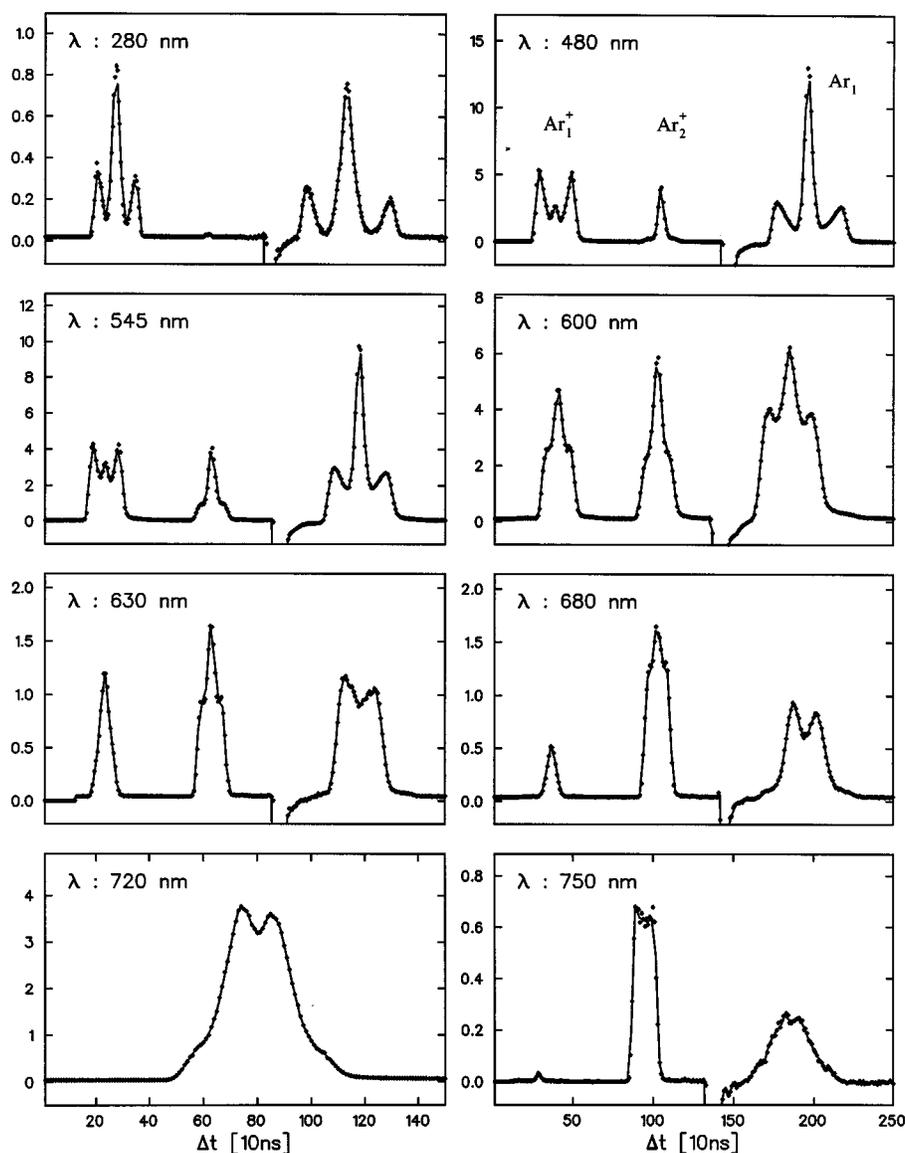
FIG. 3. Fragment TOF spectra of Ar_4^+ for different wavelengths, laser polarization parallel to the beam. The appearing fragments from left to right are Ar_1^+, Ar_2^+, and neutral Ar_1. The peak of the unfragmented Ar_4^+ is suppressed.

fragments for wavelengths above 680 nm. A spectra measured exclusively for the neutral fragments at 720 nm is shown in Fig. 3.

Here in addition to the inner wings already described two outer wings are visible, which indicate particles with velocities of $\bar{v} = 1800$ m/s ($\sigma = 340$ m/s). It was carefully checked by variation of the laser intensity that these outer wings are not due to two-photon absorption. Obviously a fragmentation channel exists where the inner energy of the tetramer is effectively transformed into translation kinetic energy of one ejected atom. Apart from this speciality the ionized argon tetramers behave very much like the xenon ones.

IV. DISCUSSION

Xe_3^+ exhibits the fragmentation pattern of a linear molecule with a transition moment parallel to its axis and a totally repulsive excited state.[11] It is thus very similar to Ar_3^+, for which such a pattern has been observed in a number of

experiments[12–14] and explained by simulations.[15,16] Upon fragmentation of the linear xenon trimer the outer two particles gain high velocities in the direction of the laser polarization, while the center particle only gains a low velocity; as for this one the repulsion forces mainly cancel out. The positive charge generally tends to localize on the outer fast particles, as can be explained by the symmetry of the wavefunction of the excited state.[11] At a photon wavelength of about 380 nm, however, due to an avoided crossing in the potential curves, a large amount of slow ions are produced.[11] This avoided crossing is responsible for the dramatic change of the fragmentation pattern within a relatively narrow photon energy range, which can be used as a fingerprint of the linear Xe_3^+.

The fact that the same change in the fragmentation pattern can be observed for the xenon tetramer thus proves that the ionized tetramer consists of a linear ionized trimer with an additional atom attached. As this atom obviously does not change the electronic states of the trimer core, it should just be bound by polarization forces at a long bonding distance.
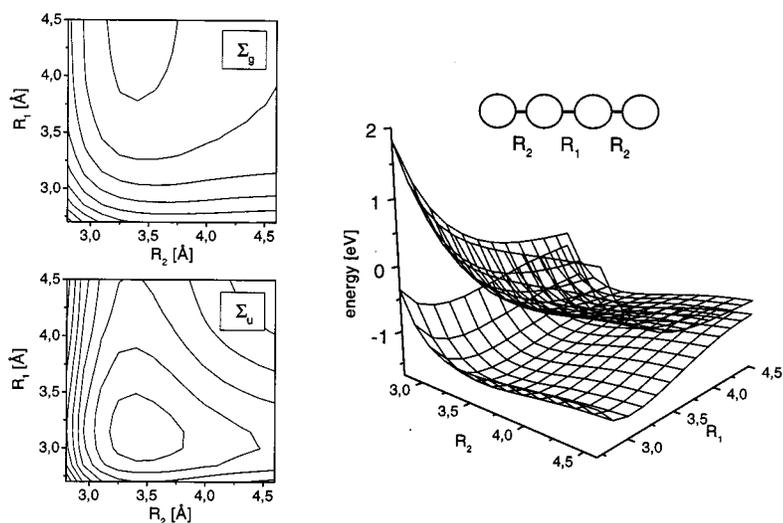
FIG. 4. Calculated potential surfaces for the Σ_u ground state and the first excited Σ_g state of Xe_4^+ in $D_{\infty h}$ symmetry (see Ref. 18).

This is exactly what has been predicted as a possible structure of the tetramer.[2,17]

In the course of the fragmentation this additional atom will not experience strong forces and hence will not gain high velocities. In the case of total fragmentation it will thus just add to the intensity of the slow neutral monomer fragments. There is, however, a second possibility for the fragmentation of such a T-shaped tetramer. If the ionized trimer core fragments in a way that the inner, slow atom obtains the positive charge, it can form a bound dimer with the spectator atom. This dimer fragment will have a low center-of-mass velocity, as the ones observed around 370 nm. In this wavelength region hence the Xe_2^+ fragments are formed by charge redistribution. We will not discuss this process in detail here, but want to hint at an interesting peculiarity: it can be deduced from the potential energy curves of Xe_3^+ as given, for example, in Ref. 11 that in the wavelength region around 370 nm after fragmentation of the trimer the ion monomer fragment will be in the excited fine structure state $P_{1/2}$. The newly formed dimer fragment will thus not be in the ground state, but in the excited $\Pi(1/2)_u$ state, which is bound as well. This formation of an excited dimer obviously is more favorable than the formation of a dimer out of ground state ion and the spectator atom, as at 540 nm, although slow ions do appear, no dimer fragments can be observed. In this case the spectator atom seems to experience a slight repulsion.

In contrast to higher photon energies, at the lowest photon energy the fragmentation pattern of the tetramer clearly differs from that of the trimer. While Xe_3^+ at 770 nm exhibits almost the same pattern as at 365 nm, the pattern of Xe_4^+ at 770 nm can only be explained by the breakup of the tetramer into two dimers.

A tetramer structure has thus to be found, the excited state of which tends to fragment in such a way. It seems to be very unlikely that during fragmentation of the T-shaped structure the two neutral fragments will be ejected into the same direction and with similar velocities. For a linear structure, however, this is quite possible, as will be explained.

Linear symmetric Xe_4^+ has a Σ_u ground state. In the near infrared the dominant excited state is the lowest Σ_g state. In

Fig. 4 the corresponding potential surfaces are shown. The potential energy surfaces indicate that the excited Σ_g state is repulsive in the R_1 coordinate, which is the bond distance of the two inner atoms, but bound in the R_2 coordinate, which is the bond distance of the outer dimers. So upon excitation the tetramer will start to fragment into two bound dimers, until at a larger distance the positive charge localizes on one of the dimers. Hereby the bond of the other dimer will become slightly repulsive, so that a bound ionized dimer will be ejected into one direction, and two neutral atoms with a small relative velocity into the opposite one.

There is a simple qualitative reason for this form of the potential energy surface, which has its origin in the character of the electronic wavefunctions. In Fig. 5 a LCAO (linear combination of atomic orbitals) representation of the σ valence molecular orbitals of linear Xe_4^+ or Ar_4^+ are schematically shown. These four orbitals are filled with seven electrons (the eight π-orbitals, which are not shown, taking up 16 electrons). In the electronic ground state all orbitals except the highest σ_u orbital are doubly occupied, which produces a Σ_u state. The transition to the dominant excited Σ_g state takes place by transferring one electron from the upper σ_g orbital to the upper σ_u orbital.

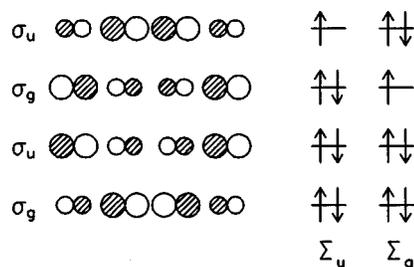A qualitative determination of the bonding character of

FIG. 5. LCAO representation of the lowest four σ molecular orbitals of linear symmetric Xe_4^+ formed out of the valence p orbitals of the atoms. On the left the molecular orbitals are shown; on the right the population of the orbitals is given for the Σ_u ground state and the first excited Σ_g state of the molecule. Not shown are the π molecular orbitals, which take up another sixteen electrons.

these states can be made by examining the orbital of the missing electron. As for the neutral tetramer the contributions of all electrons add up to a nonbonding character, it is sufficient to know the character of the orbital for which the electron is missing. In the ground state this hole orbital (the upper σ_u orbital) has a node between every two atoms, that is, it is totally repulsive. A missing electron here leads to a bound molecular state. In the excited Σ_g state the hole orbital still has nodes between the outer atoms and the inner ones, but not between the two inner atoms. In this state the inner bond is repulsive and the outer ones bound, as we wanted to show.

It has to be noted that this discussion still holds if the ground state has a distorted symmetry, that is, if the two bond lengths R_2 are not equal. In such a configuration in the ground state the positive charge would mainly reside on the three atoms which are closer together, while in the excited state some of the charge would be transferred to the outer atom. Nevertheless the character of the wavefunctions will be very similar, so that such a distorted tetramer will also fragment into two dimers.

Summarizing these results, one can state that while at higher photon energies the fragmentation pattern of the tetramer resembles that of a T-shaped cluster, at lower photon energies it resembles that of a linear isomer. This means that both isomers exist in the beam, and that the linear isomers absorb at lower photon energies than the T-shaped ones. From the measured photoabsorption cross sections[7] one can thus deduce that the T-shaped isomer by far is the dominant structure.

The photofragment spectra of the argon tetramers exhibit the same behavior, though not as clearly. Here again at the higher photon energies the fragmentation pattern is very similar to that of the trimer,[11] while at the lowest photon energies again a break-up into two dimers can be observed. The overall properties of ionized argon clusters are very similar to those of xenon ones. Apart from the much larger spin orbit coupling in the case of xenon their potential energy surfaces have the same characteristics. Thus the same as said for the xenon tetramer holds for the argon tetramer as well: the fragmentation pattern of the energetically favored T-shaped structure will be similar to that of the trimer, while the linear Ar_4^+ isomer will fragment into two dimers. From the observations one thus can again deduce that these two isomers are present in the beam.

Although they do not seem to be the dominant structure, it is remarkable that linear isomers exist and that they have different electronic properties. This sheds some light on the discussion of the structure of the ionized core in rare gas clusters. As already linear tetramers exist, also for larger clusters isomers with linear tetramer cores should be present in the beam.

In the case of ionized helium clusters this was shown recently. Although the tetramer itself only seems to have the T-shaped structure, it was demonstrated that for clusters with 8–10 atoms isomers with linear tetramer cores exist.[9]

V. SUMMARY

The center-of-mass velocity distributions of all ionized and neutral fragments of Xe_4^+ and Ar_4^+ have been measured for a broad range of photon energies. The distributions show distinct structures, which allow to determine the geometries of the clusters. For both clusters the dominant structure seems to be that of a charged linear trimer with an additional neutral atom attached to its side, as has been predicted by theory and deduced from absorption cross-section measurements. In this experiment it could be demonstrated that additionally there are clusters present in the beam which have a linear structure. These clusters have a different absorption spectrum, and they exhibit a different, characteristic fragmentation pattern.

ACKNOWLEDGMENT

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