Z. Phys. B 98, 417–419 (1995)

ZEITSCHRIFT
FÜR PHYSIK B

Cold Ar_3^+ generated by ionization of argon clusters in large helium clusters: temperature dependence of the photofragmentation

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Abstract. Ionized argon clusters were generated by electron impact ionization of neutral argon clusters embedded in large neutral helium clusters. Photofragmentation spectroscopy of Ar_3^+ and Ar_3^+He produced in this way demonstrates the strong influence of vibrational excitation on the photodissociation dynamics, and indicates the low internal energy of the latter cluster.

PACS: 36.40.Mr; 36.40.Qv; 67.55.Lf

I. Introduction

The positively charged argon trimer is a well examined molecule. Several groups have studied the wavelength dependence of its photoabsorption cross sections [1, 2, 3] as well as the kinetic energy release to the photofragments [4, 5, 6]. The experimental findings are consistent with the properties calculated for a linear symmetric trimer. The dominant optical transition is identified as the transition $\Sigma_u \rightarrow \Sigma_g$. The excited state is totally repulsive, and so in the course of the fragmentation the outer atoms of the linear trimer gain high velocities in opposite directions. The middle atom, for which the repulsion forces mainly cancel out, does not pick up much momentum. Thus the photoexcited trimer fragments into two fast particles with opposite velocities and one slow particle. In the excited gerade-state due to its symmetry there is a vanishing probability for the positive charge to be located on the middle atom. If this charge distribution is maintained in the course of the dissociation, one slow neutral atom, one fast neutral atom and one fast ion should be produced. In the measurements of the kinetic energy release, however, additionally a small amount of slow ions could be observed, the origin of which has been subject to a vivid discussion. It was proposed [7, 8] that in the course of the fragmentation nonadiabatic transitions between gerade- and ungerade-states take place at large interatomic distances. This transitions are possible if the $D_{\infty h}$-symmetry is disturbed by nonsymmetrical vibrational modes. On the other hand very recent experiments on Xe_3^+ yield strong evidence that slow ions are dominantly produced due to adiabatic passage through avoided crossings, which are caused by spin-orbit-coupling together with nonsymmetrical vibrational modes [9]. Both models require a vibrational excitation for the production of the slow ions. Up to now no experiments studying the influence of the internal energy on the trimer photofragmentation dynamics are available, since vibrationally cold ionized rare gas clusters generally are difficult to produce. In the standard production method via the ionization of free neutral clusters the ions always are vibrationally excited because of the large difference between the bond lengths in neutral and ionized clusters. If, however, the ionization takes place inside a helium cluster, the internal energy of the ionized argon cluster is transfered to the helium cluster and released up by evaporation of helium atoms. In this way in principle very cold rare gas clusters ions can be produced.

In the present report we compare experiments performed on pure, possibly strongly vibrationally excited Ar_3^+, and Ar_3^+He. For the latter species an upper limit of the internal energy is given by the binding energy of the helium atom to the argon trimer. This value is not exactly known, but certainly will be equal to or less than the binding energy of a helium atom to a charged linear helium trimer, which is about 30 meV [10].

II. Experimental

The experiments were performed in a tandem time-of-flight mass spectrometer. Neutral helium clusters were produced in a low temperature supersonic expansion, and after passing a skimmer the clusters were ionized by electron impact. Argon atoms were embedded into the helium clusters by applying a argon background pressure of

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about 2×10^{-4} mbar to the second chamber, in which the helium clusters cover a flight path of about 50 mm between skimmer and electron beam. The ionized clusters were then mass selected in a reflectron time-of-flight mass spectrometer (TOF-MS). Selected sizes were extracted into a secondary, linear TOF-MS. Here the clusters were irradiated by a pulsed polarized laser beam after acceleration, so that the center-of-mass velocities of the fragments can be determined from the distribution of their

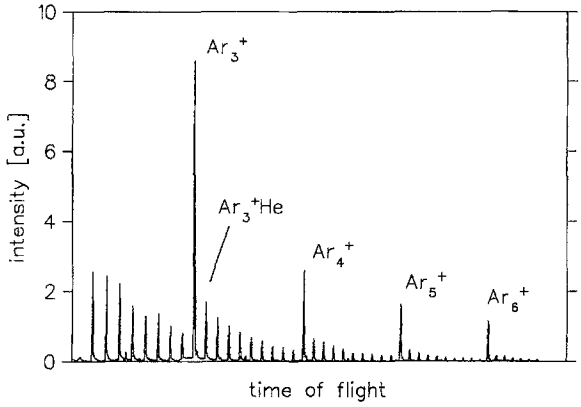

Fig. 1. Mass spectrum obtained by electron impact ionization of large helium clusters ($\langle N \rangle \approx 7000$) doped with argon atoms. The photofragmentation experiment was performed on the indicated species Ar_3^+ and Ar_3^+He

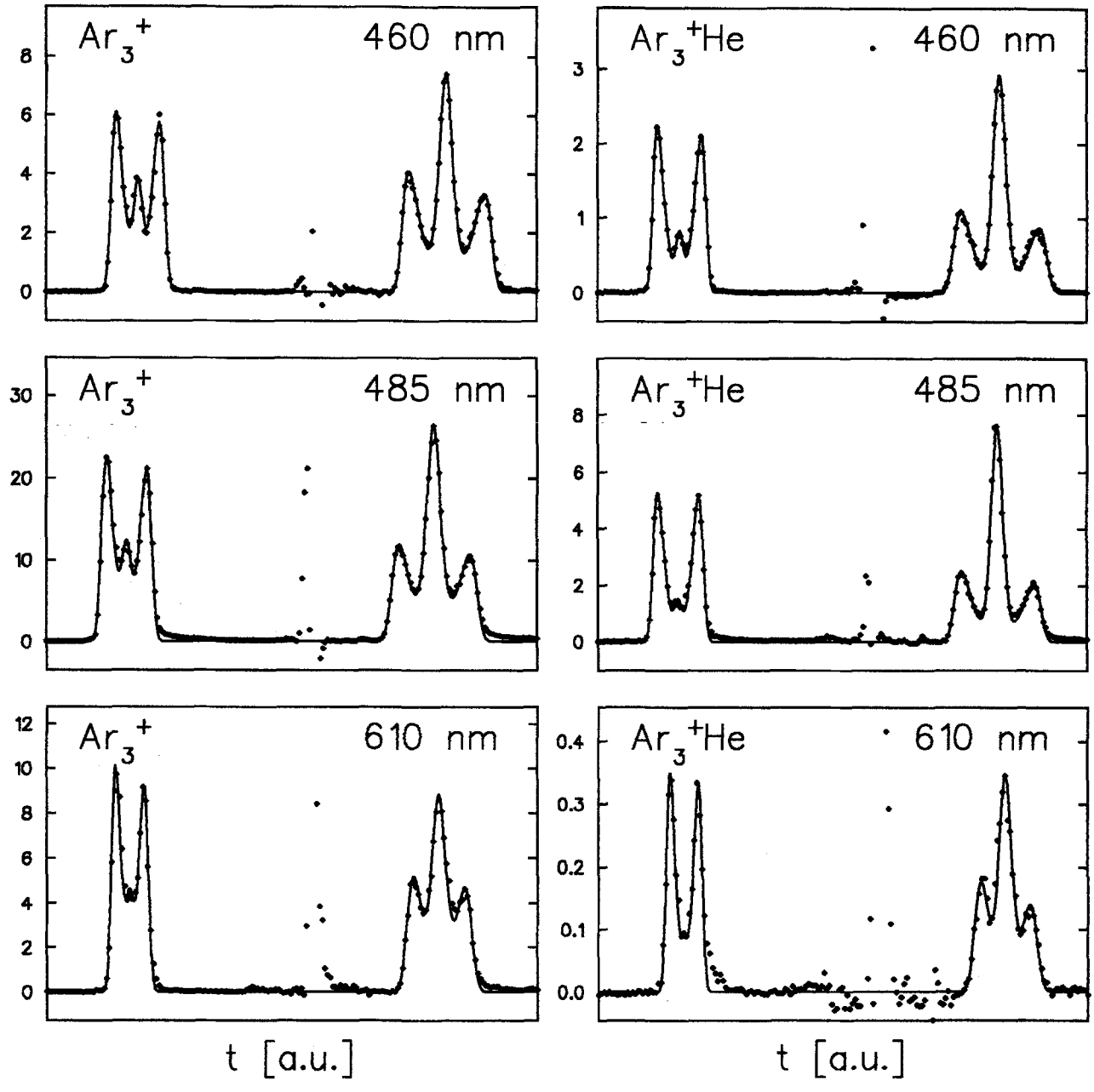

Fig. 2. Fragment time-of-flight spectra after photodissociation of Ar_3^+ and Ar_3^+He at three different wavelengths. The polarization of the laser was parallel to the beam axis. See the text for detail

arrival times. A weak acceleration behind the laser interaction region served to separate fragments of different sizes. The experimental method and the apparatus are described in detail in [9, 11].

III. Results and discussion

A typical mass spectrum obtained by ionization of argon clusters embedded in helium clusters is displayed in Fig. 1. The dominant species are pure ionized argon clusters Ar_k^+, but mixed clusters $Ar_k^+ He_l$ can be seen as well. Time-of-flight spectra of the clusters Ar_3^+ and $Ar_3^+ He$ following laser excitation at 460 nm, 485 nm, and 610 nm are shown in Fig. 2. The laser polarization was parallel to the beam axis in all three cases. In the spectra from left to right the ionized monomers appear before the neutral monomers. Ionized dimers are not produced in this wavelength region, and the peak of the unfragmented parent clusters have been supressed here by subtracting spectra measured without laser excitation. The TOF peaks of both fragments exhibit a similar structure. They consist of a central peak and a pair of wings. The central peak can be attributed to the middle atom of the linear trimer, which does not gain much velocity by the fragmentation process, while the wings can be attributed to the two outer particles which have picked up a high velocity (about 1600 m/s at 485 nm) in direction of the laser polarization, that is in and against the flight direction of the cluster. The most interesting feature here is the intensity of the slow ions relative to that of the fast ones. In the case of the Ar_3^+ this ratio is the same as is observed for fragmentation of a trimer produced by the standard method, whereas in the case of $Ar_3^+ He$ the relative abundance of the slow ions is strongly reduced. Two possible reasons for this reduction of the slow ion intensity have to be discussed: it could either be due to the probably reduced vibrational excitation of the argon trimer in the case of the $Ar_3^+ He$, or the attached helium atom could be responsible for it.

This latter explanation seems to be very unlikely, as because of the large difference in the ionization potentials of argon and helium atoms no charge can be transfered to the attached helium atom, i.e. it can be considered as a spectator atom which only interacts with the trimer via its very small polarizability. Moreover, an influence of the He atom would rather increase the slow ion intensity than reduce it, as was observed recently for the case of the photofragmentation of He_3^+ and He_4^+. He_4^+ consists of a linear charged trimer with a loosely attached helium atom, and here the attached atom indeed strongly increases the abundance of the slow ions [11].

So we can safely assume that the reduction of the slow ion intensity is not caused by the attached He atom, but instead is due to the reduced internal energy of the Ar_3^+. Thus the experiment on the $Ar_3^+ He$ can be looked upon as a measurement on a free argon trimer, where the attached helium atom only serves as an indicator for the internal energy.

The results demonstrate the importance of the vibrational excitation for the dissociation dynamics of the argon trimer. Of course they cannot decide which of the two mechanism discussed in the introduction is responsible for the appearance of slow ions, since for both vibrational excitation play a crucial role.

We thank J.P. Toennies for enlightning discussions about He clusters. This work has been partially supported by the Deutsche Forschungsgemeinschaft through SFB 276, TP C5.

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