Measurement of thermal energy charge transfer rate of multiply charged molybdenum (molybdenum(6+)) and argon

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Measurement of thermal energy charge transfer rate of multiply charged molybdenum ($\text{Mo}^{6+}$) and argon

Jiang, Ying, M.S.
University of Nevada, Las Vegas, 1990
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MEASUREMENT OF THERMAL ENERGY CHARGE TRANSFER RATE
OF MULTIPLY CHARGED MOLYBDENUM (Mo$^{6+}$) AND ARGON

By
Ying Jiang

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

in

Physics

Department of Physics
University of Nevada, Las Vegas
July, 1990
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University of Nevada, Las Vegas
July, 1990
MEASUREMENT OF THERMAL ENERGY CHARGE TRANSFER RATE
OF MULTIPLY CHARGED MOLYBDENUM (Mo\textsuperscript{6+}) AND ARGON

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ABSTRACT

We have made the first measurement of the thermal energy charge transfer rate of Mo\textsuperscript{6+} and neutral argon. This measurement was carried out using a technique that combines the production of ions by laser ablation and an ion trap. The multiply charged ions produced by laser ablation are cooled by crossed beams collision. These ions are stored in a radio–frequency ion trap. The charge transfer rate is determined by measuring the rate of loss of stored ions in the trap. The charge transfer rate coefficient, \( k \), of Mo\textsuperscript{6+} and Ar is \( 1.02(10) \times 10^{-10} \text{ cm s}^{-1} \). The estimated uncertainty is \( \pm 10\% \) and is mainly due to the uncertainty in the argon density determination and the statistical fluctuation of the ion signals.
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I. INTRODUCTION

Thermal energy charge transfer between multiply charged ions and neutrals has proven to be one of the most difficult basic collision processes to predict reliably and yet it plays an important part in the evolution of many physical systems. In addition charge transfer of multicharged ions and neutrals in the low energy regime has significant applied importance, so it is surprising that there were few reported results. It is only since 1975 that some experimental and theoretical work on this important subject has appeared.¹

Major applications for thermal energy charge transfer between multiply charged ions and neutrals are:

(1) Thermonuclear fusion research:

It is important to understand the interactions among the impurity ions and neutrals at the edges of the tokamak fusion plasma. The predominant effect of impurities upon a fusion plasma is radiation cooling. This is a critical problem in thermonuclear fusion. To analyze and model these energy loss problems due to charge transfer, data for highly stripped ions of wall materials such as Cr, Fe, Ni, Mo and W are needed.²

(2) Astrophysics:

Atomic charge transfer plays an important role in cosmic plasmas. In interstellar gases composed of elements in their cosmic abundances, ionizing radiation often produces partially ionized plasmas containing some neutral atomic hydrogen. Charge transfer collisions with hydrogen drastically modifies the ionization structure of the gas.
(3) Space physics:

Electron capture by a multiply charged ion on an atom generally results in the production of a highly excited state of the daughter multiply charged ion. Radiation in the x-ray region is released as the ion relaxes to its ground state. This property is of interest as an x-ray and vacuum-ultra violet (vuv) source in the interstellar media.

(4) Short wavelength lasers:

Charge transfer plays a crucial role as a pumping mechanism for population inversion in short wavelength lasers. Knowledge of such charge transfer rates has considerable impact on studies relating to the generation of x-ray or vuv laser light.

There are two major approaches in the study of charge transfer between multiply charged ions and neutrals: 1) the ion beam approach \(^{7-9}\) and 2) the ion trap approach \(^{10-12}\). In the ion beam approach, the ion can be produced by electron cyclotron resonance (ECR), \(^{13}\) electron-beam-ion source (EBIS), \(^{14}\) or source-accelerator devices. The beam approach allows studies to be carried out at or above 0.1keV/amu. Recently, using the merged-beam technique, the study has been extended to collision energies as low as 0.9eV/amu. \(^{15}\) Due to the difficulty of measuring the relative energy between two merged beams, the uncertainty of measurement at that energy level is rather large. So far no published data of thermal charge transfer of multiply charged ions of refractory metals and neutrals has been reported. The ion source used in the ion trap approach uses electron impact dissociative ionization of a molecular gas \(^{16, 17}\) or the electron impact ionization of an atomic gas. The limited choice of a parent gas and a small dissociative ionization cross section permits the production of only a very few types of singly or multiply charged ions in sufficient quantities for study. \(^{18}\) Experiments using this technique are further complicated by the interaction of the ions with the parent source gas. Several approaches have been introduced to overcome
these limitations. An electron–beam ion trap (EBIT) has been built for the production of low–energy, very highly charged ions and the study of their collisions with electrons. However, these techniques are not well suited to the study of charge transfer between ions and neutral atoms and molecules. Kwong introduced a novel approach that combines the production of ions by laser ablation with the ion trap technique. The energy of the ions ($W^{q+}$ with $1 \leq q \leq 4$ and $Mo^{q+}$ with $1 \leq q \leq 6$) stored in the trap has been estimated to be less than $4x10^{-3}$ eV/amu.

This thesis focuses on the first measurement of the thermal energy charge transfer coefficient for $Mo^{6+}$ with Ar using this new technique. No theoretical calculation of the charge transfer rate of Ar and $Mo^{6+}$ has been made. It is hoped that the result of this experiment will stimulate further theoretical studies.

This thesis is divided into several parts. The first part gives a theoretical background of charge transfer. The second part outlines experimental facilities. The third part discusses experimental methods and procedures in some detail. The fourth part shows the experimental results and data analyses.
II THEORETICAL BACKGROUND

The charge transfer process to be considered is

\[ A^{q+} + B = A^{(q-1)+} + B^+ \]

where \( A^{q+} \) is multiply ion and \( B \) is the neutral atom. This process can also be represented by

\[ A + (B + e)_1 = (A + e)_2 + B \]

in which the active electron \( e \) is attached to state 1 in system \( B \) initially, and is attached to state 2 in system \( A \) finally.

Using quantum mechanics to describe the cross section of this charge transfer process is actually a very complex problem. It involves the finding the stationary states of a system of particles, the nuclei and the electrons, all interacting with each other. In general, it is impossible to solve the Schrodinger equation for such a system. There are however, some approximate theoretical approaches to solve this problem. At low energy (below a few keV/amu), a significant approach is the Born–Oppenheimer approximation. In this approach, the orbiting electron velocity is much larger than the collision velocity. The motion of electron and nuclei are considered separately. One begins by determining the motion of the electrons for a fixed value of the distance \( R \) between the two nuclei, thus one obtains a series of stationary states wavefunction \( \varphi_i \) for the electron system. As nuclei move closer, the electron wavefunction will change adiabatically to the corresponding state \( \varphi(R) \). The total Hamiltonian of the colliding system is divided into two parts

\[ H = H_n + H_{el} \quad (1) \]

(\( h = 1 \), atomic units are used through this part) where \( H_n \) is the nuclear Hamiltonian and \( H_{el} \) is the electronic Hamiltonian. The total wave function \( \Psi(t) \) satisfies the time–dependent Schrodinger equation
Each state of multiply-ionized systems before and after charge transfer can be described by a potential energy curve. The initial state potential curve can be approximated by a constant term plus an attractive induced polarization, \((qe)^2 \alpha R^{-4}\), where \(\alpha\) is the dipole polarizability of B. The final state curve is approximated by a constant term plus a Coulomb-repulsion term \(\frac{(Q-1)e^2}{R}\).

Figure 1 is the schematic representation of the potential energy curves for a multiply-charged system. \(R_c\) is the curve-crossing point. Curve-crossing methods have been used extensively to estimate cross sections. One of the methods is the Landau-Zener method. It asserts that the charge transfer process only occurs to an appreciable extent in a very narrow zone around the potential curve crossing point \(R_c\). Therefore, the total cross section can be derived by

\[
\sigma = 2\pi \int_0^{R_c+\delta} P(b) b \, db
\]  

where \(b\) is the impact parameter (see Fig. (2)). \(P(b)\) is the transition probability between two states. \(P(b)\) is not zero only if \(b\) is within the region of \(R_c \pm \delta\). This transition probability can be obtained by solving the Schrödinger equation of the system. In the simplest case we consider, \(A + (B + e)_1 = (A + e)_2 + B\), the wavefunction is the linear combination of the wavefunctions of initial state \(\psi_1\) and final state \(\psi_2\). Using the time dependent version of the semi-classical formalism, the total wavefunction is

\[
\psi(t) = \frac{\sum a_i(t) \phi_i(R, \vec{r}) e^{-i \frac{1}{\hbar} \int t \, e_i(R(t')) \, dt'}}{2\pi \int_0^{R_c+\delta} P(b) b \, db}
\]  

where \(i = 1, 2\), and \(|a_i(t)|^2\) represents the probability that the colliding system is in the state \(i\) at time \(t\). Substituting equation (4) into the Schrödinger equation (2), one gets the two coupled equations
Fig. (1) Schematic representation of potential energy curves for a multiply-charged system.

Fig. (2) Classical collision trajectory.
\[ \frac{da_1(t)}{dt} = a_2(t)\epsilon_{12}(R)e^{-ij\Delta \epsilon} dt \]
\[ \frac{da_2(t)}{dt} = a_1(t)\epsilon_{12}(R)e^{-ij\Delta \epsilon} dt \]

where \( \Delta \epsilon = \epsilon_1(R) - \epsilon_2(R) \) is the energy separation between the initial (state 1) and final (state 2) states and \( \epsilon_{12}(R) \) is the interaction potential between these two states. In many cases of practical interest, the coupling between many states can be seen as successive sets of couplings between two states. The boundary conditions appropriate to the process being considered are

\[ a_1(-\infty) = 1, \quad a_2(-\infty) = 0 \]

If we know \( \Delta \epsilon \) and \( \epsilon_{12}(R) \), we can compute the transition probabilities from Eq.(5)

\[ P = |a_2(+\infty)|^2 = 1 - |a_1(+\infty)|^2 \]

Then one may obtain the total cross section.

The Landau–Zener model supposes that the transition region is so small that the \( \Delta \epsilon = \epsilon_1 - \epsilon_2 \) can be considered as a linear function of time

\[ \Delta \epsilon = \epsilon_1 - \epsilon_2 = \lambda t \]

Furthermore, the interaction potential is assumed to be constant and equal to its value at \( R_c \)

\[ \epsilon_{12}(R) = \epsilon_{12}(R_c) = \beta \]

where \( \lambda \) and \( \beta \) are constants. The transition probability calculated by Zener is

\[ P = \exp(-2\pi\kappa), \text{ with } \kappa = \epsilon_{12}/|\frac{d}{dt}(\epsilon_1 - \epsilon_2)| \]

In many real collision processes, transitions may occur well away from the crossing. It restricts the range of validity of this model. A more rigorous approach used to calculate accurate cross sections at low energy is the perturbed–stationary state (PSS) method. We shall not discuss it in this thesis since it is beyond the scope of this work.
III. EXPERIMENTAL FACILITIES

The facilities for measuring the Mo\(^{6+}\) charge transfer rate include a Nd:YAG laser to create the molybdenum ions, a vacuum chamber with standard pumping system, an rf–quadrupole ion trap, an ion detection system, a timing control system, and a data acquisition system. Figure 3 is a block diagram of the facilities used.

1. Laser Ablation Ion Source

A diagram of the laser ablation ion source is shown in Fig.4. Two molybdenum targets attached to a stainless steel mount are used to produce molybdenum ions. Between each molybdenum target and the ion trap, a stainless steel skimmer with a 4mm diameter hole cut at the center is positioned to collimate the expanding ion cloud produced by laser ablation into a narrow cone. This minimizes back scattering of ions from the expanding ion cloud by preventing them from striking the ring electrode or its mounting structure. Four 5mm diameter holes are cut at the ring electrode of the ion trap to let the ions stream into the trap and the laser beam to pass through the trap unobstructively. A Langmuir probe is installed outside of the ion trap near the ring electrode for diagnostic purposes. Each target assembly (molybdenum target, target mounting plate and skimmer) is held in position in the plane of the ring electrode and at the same fixed distance from its center by two stainless steel studs attached to the ion trap support structure. This arrangement minimizes the scattering of ions from the wall of the trap's ring electrode as they expand into and pass through the ion trap. The laser axes, perpendicular to the surface of each target, intersect each other at right angles at the center of the ion trap.

Two groups of ions are generated by simultaneous ablation of the two molybdenum targets by two laser beams. These two laser beams are obtained by
Fig. (3) Block diagram for Mo$^{6+}$ + Ar charge transfer experiment.
Fig. (4) Diagram of laser ablation and ion trap facility.
splitting the output of the second harmonic of a Nd:YAG laser (Molelectron MY-32 Oscillator/Amplifier System) by a 50/50 dielectric coated beam splitter. These two pulsed laser beams are collimated, so that they pass through the holes cut out at the ring electrode and strike the targets unscattered. Each ablation beam is focused by a 25cm focal length convex lens positioned outside the vacuum chamber. Fine focusing of each laser beam on the target surface is achieved by translating the lens along the laser axis until plasma formation is observed. Plasma formation can be detected visually by using a notch filter that blocks scattered light at the wavelength of laser beam. Each laser pulse has about 20mJ of energy, a time duration of 25ns, FWHM (full width at half maximum), and a spot size at the ablation target of about 0.1mm. The mean power density of the ablation laser at the target surface is estimated to be about 1.2x10^9 W/cm². The mean kinetic energy of the laser induced ions is measured by a Langmuir probe. The mean energy of the laser induced plasma ions is estimated about 250eV. This value is much larger than the highest trapping potential of 22.3eV used in this experiment.

2. The Vacuum System

The vacuum system provides a high vacuum environment for the experiment in order to minimize the influence of impurity gas on our experimental results.

As shown in Fig. (5), the ion trap assembly, which consists of an ion trap, electron gun, deflection plate and channel electron multiplier (CEM), is mounted inside the vacuum chamber. The vacuum chamber is pumped by a Varian VHS–4 diffusion pump backed by a mechanical pump. A liquid nitrogen cold trap is placed between the chamber and the diffusion pump to minimize back streaming of oil molecules from the diffusion pump and the mechanical pump. A Micromass foreline trap is placed in the foreline to further prevent mechanical pump oil from streaming into the diffusion pump (see Fig.6).
Fig. (5) The vacuum chamber and the ion trap
Fig. (6) The vacuum system.
A gate valve with a thermocouple (TC) gauge is positioned between the diffusion pump and the mechanical pump. This pneumatic valve is driven by high pressure nitrogen gas. It automatically isolates the vacuum chamber, cold trap and diffusion pump from the mechanical pump when the foreline pressure measured by the TC gauge exceeds a preset threshold. This protects the diffusion pump from being damaged due to foreline vacuum failure. The threshold is usually set to 40 mTorr. The diffusion pump is further protected by the automatic shutdown system which consists of a electronic control switching circuit, a cooling water flow sensor switch, and the foreline TC gauge mentioned above. The diffusion pump shuts off to minimize the diffusion pump oil from entering the vacuum chamber when one of the following events occurs:

i). The main power to the vacuum is shut off for more than 15 seconds.

ii). High pressure (about 40 mTorr) at the mechanical pump is reached.

iii). The cooling water for diffusion pump runs below an acceptable level for cooling.

The stainless steel ultra-high vacuum chamber has six ports. The low port is connected to the cold trap and vacuum pump system. The top and front ports are sealed by 20cm conflat flanges and each has a Pyrex window for the passage of two laser beams. The back port is connected to a leak valve and a residual gas analyser (Masstorr DX100). The residual gas analyser (RGA) is used to measure the pressure in the chamber. One of the two side ports is used for mounting the ion trap assembly and electrical feedthrough, while the other is for mounting the channel electron multiplier.

With this vacuum system, a residual background pressure of $1 \times 10^{-9}$ Torr (mainly water and molecular hydrogen) can be obtained without baking. Background pressure of at least a factor of 10 lower can be reached after baking the system. No baking was carried out in this experiment.
3. Ion Trap Assembly

1) Ion Trap

The ion trap is the key component of the apparatus for this experiment. It provides a relatively weak field (50V/cm) to confine the desired ions. The ion trap used in our experiment is a radio–frequency quadrupole trap. Stainless steel mesh was used to make the ion trap because of its strength in maintaining a rigid structure and because it is transparent to gas molecules. The configuration of the ion trap used in this work is shown in Fig. (7). The rf trap is made up of a cylindrical ring electrode and two flat end caps. The radius of the ring electrode is 1.67cm and the length is 3.34cm. The diameter of the two flat end caps is 3.40cm. We chose this design because of its simplicity in fabrication. Both the ring electrode and the end caps are made from 30 gauge 304 stainless steel mesh.

Several studies have been made on the properties and characteristics of the quadrupole trap. These studies concentrated on ion traps with hyperbolic electrodes. The first theoretical study of a cylindrical ion trap was carried out by Benilar and Audoin in 1973. Unlike the trap with hyperbolic electrodes, there is no simple solution for the potential distribution of a cylindrical trap. However, it has been shown that the potential distribution near the center of a cylindrical trap approximates that of an ideal hyperbolic trap. We shall adopt the solution that gives the ion trajectory in the hyperbolic trap as the solution in the cylindrical trap. We shall confirm this assumption in chapter IV section 3. The stable trajectories of the stored ions in a periodic hyperbolic potential can be obtained from the solution of the Mathieu equation

\[
\frac{d^2u}{dv^2} + (a - 2qcos2v)u = 0
\]

where \( v = \frac{\Omega t}{2} \)

The two parameters \( q \) and \( a \) determining the ion trajectories are related to the ion
Fig. (7) Configuration of the ion trap.
charge state $q$, mass $m$, the trap's length $2z_0$, the trap's radius $r_0$, rf frequency $\Omega$, rf amplitude $V_0$ and dc bias $U_0$. The relations are

$$2q_r = -q_z = \frac{8qV_o}{m(r_0^2 + 2z_0^2)\Omega^2}$$

$$2a_r = -a_z = \frac{16qU_0}{m(r_0^2 + 2z_0^2)\Omega^2}$$

Figure 8 shows the stability diagram obtained by requiring the values of $q_z$, $q_r$, $a_z$, and $a_r$ to be such that the motion is stable in both the axial and radial directions. For an ion of fixed $q/m$, the values of the trap voltages ($V_0$, $U_0$) and frequency ($\Omega$) selected determine the location of the operating point in this diagram. Only if the operating point of an ion is in the interior of the closed region, trapping can occur.

From the Mathieu equation, the potential well depths in the axial and radial direction are obtained

$$D_z = \left[ \frac{4qV_o}{m(r_0^2 + 2z_0^2)\Omega^2} - \frac{2U_0}{(r_0^2 + 2z_0^2)} \right] z_0^2$$

$$D_r = \left[ \frac{qV_o}{m(r_0^2 + 2z_0^2)\Omega^2} + \frac{U_0}{(r_0^2 + 2z_0^2)} \right] r_0^2$$

For a spherical well, we have $D_z = D_r = D$. For our trap design $r_0 = z_0 = 1.67\,\text{cm}$, we get

$$D = \frac{2}{3}U_0$$

which means that the spherical potential well depth is directly proportional to the dc bias of the ion trap.
The optimum trapping parameters have been investigated both theoretically and experimentally.\textsuperscript{26, 27} Fig.(9) is the three dimensional stability diagram of the cylindrical trap. The optimum trapping region is between \( q_z = 0.55 \) and 0.60 near the spherical well line. For a fixed \( q_z \) (or \( a_z \)), the value of \( a_z \) (or \( q_z \)) which results in a spherical potential well will give maximum stability. We have used \( N^2^+ \), \( N^+ \), \( Ar^{2^+} \), and \( Ar^+ \) to test the storage characteristics of our rf cylindrical trap. The regions of stability observed were found to be consistent with the theoretical calculations for a trap with hyperbolic electrodes. We used the stability diagram for an ideal hyperbolic electrode trap to guide us in ion selection. We shall discuss this further in chapter IV.

2) Electron Gun and Deflection Plates

The electron gun is screw fixed to a stainless steel support and mounted outside the trap next to one of the end caps (see Fig.(5)). The electron gun used is a 7mm long, 3mm diameter tungsten dispenser cathode. It will allow higher emission current densities at a lower operating temperature. Porous tungsten with a formula of barium oxide dispersed through the matrix is the essential form of these dispenser cathodes. The electron gun is primarily used to generate ions from atomic and molecular gases to test the operation and to check the characteristics of the trap. It is also used to calibrate the system using an ion–neutral pair of known charge transfer rate. It is not used when the laser ablation ion source is used.

A pair of deflection plates is mounted between the right end cap and the channel electron multiplier (CEM). The deflection plate is gated by a switching circuit controlled by the central processing unit (CPU) which we will discuss later in section 5. When the electron gun or laser is on potentials are applied to the plates to prevent ions from reaching the detector and causing permanent damage.

The ion trap is enclosed in a grounded Faraday cage made of stainless steel mesh, which minimizes the interference of the rf field on the expansion of the laser
Fig. (8) Stability diagram of the ion trap.
Fig. (9) Three dimensional stability diagram of the cylindrical trap used in the experiment. The number of the trapped ions is the function of $a_z$ and $q_z$. 
induced ions as they drift towards the trap's ring electrode.

4. Ion Detection System

A high current channel electron multiplier (CEM) (Galileo model No.4816) has been used to detect ions confined in the ion trap. (see Fig. (5)) The channel electron multiplier is a nonmagnetic device fabricated from a special formulation of heavily lead-doped glass. When properly processed, the glass exhibits useful secondary emissive and resistive characteristics. Typically, the CEM exhibits resistance in the range of $10^8$ to $10^9$ ohms. Electrical contacts, usually chrome, are deposited onto both ends of the channel. This allows good electrical contact between an external voltage source and the CEM. Between the ends of the multiplier, a potential of a few thousand volts is applied. A particle which has enough energy will be detected when it is incident upon the interior surface of the CEM aperture and amplified by means of secondary emission. This secondary electron is accelerated by the electrostatic field within the channel until it hits the interior surface of the channel.

Two methods of mass identification have been used: Time-of-flight (TOF) of the ions and the stability diagram of the ion trap. The time of flight, $t$, is given by the equation:

$$t = s \frac{m}{2qV}$$

where $s$ is the distance between the center of the trap to the CEM, $V$ is dump pulse voltage, and $m/q$ is mass-to-charge ratio of the ions. Since all ions pulsed out of the trap have the same extraction potential, the TOF of the ions is a function of the mass-to-charge ratio ($m/q$). The TOF spectrum is digitized by a DCS-01 Tektronix digitizing camera system and sent directly into an IBM AT computer for storage and analysis. Figure 10 gives the TOF spectrum of $N^{2+}$ and $N^+$. The second method is to identify ions with the aid of the trap's stability
Fig. (10) TOF spectrum of $\text{N}^{2+}$ and $\text{N}^+$. 
diagram. The theoretical stability diagram for the ions is obtained from the solution of the Mathieu equation for the trajectories of ions in a periodic hyperbolic potential. Adjusting the \( a_z \) and \( q_z \) can shift the operating point for a particular ion in the stability diagram (see Fig.(11)). We can exclude ions of higher mass-to-charge ratio \( (m/q) \) by shifting the operating point of these ions below the edge of the stable region. All the data used in our final analysis were obtained with a CEM TOF detector. The time-of-flight spectrum is consistent with the stability diagram of the trap's behavior (see Fig.(11)).

5. Experimental Timing Electronics

Proper operation of the apparatus requires that a series of timing pulses be applied to the electrodes, the deflection plate and the data acquisition instrument. The appropriate signals are controlled by a central processing unit (CPU) which consists of an LM555 oscillator that provides the basic clock pulses and logic circuitry generating 4 TTL logic pulses. The timing diagram is outlined in Fig.(12). The first pulse prepares the Nd:YAG laser in the single shot mode. The trailing edge of the first pulse triggers the second control pulse that initiates the laser flashlamp. Following the falling edge of the laser flashlamp pulse is the third control pulse that turns on the gate switch of the CEM. The CEM is gated on only after the laser flashlamp terminates and before the next laser shot. The fourth controlled pulse initiates the extraction of ions from the trap. This dumped pulse is synchronized to a specific phase of the rf waveform so that ions are subject to the same effective extraction potential each time they are dump from the trap. This minimizes the fluctuations in the ion signals. The time between the laser shot and the dump pulse can be adjusted by a counter.

6. Data Acquisition System.

Figure 13 shows the data-acquisition system used in this experiment. The
output from the anode of the CEM is directly sent to the 7A26 vertical amplifier in a Tektronix 7104 oscilloscope. The scope sweep is triggered by the leading edge of the ion dump pulse. The ion's TOF spectrum is digitized by DCS–01 Tektronix digitizing camera system. The spectrum is fed directly into an IBM AT computer for storage and data analysis.
Fig. (11) Stability diagram and TOF spectrum of $N_2^+$ and $N^+$ with different values of $a_z$ and $q_z$. (a) Calculated results show that at $\Omega = 0.65$ MHz, $V_o = 225$ V, $U_o = 20$ V, only $N_2^+$ can be trapped. (b) $N_2^+$ TOF spectrum at $\Omega = 0.65$ MHz, $V_o = 255$ V, $U_o = 20$ V.
(continued) (c) Calculated results show that at $\Omega = 1.2\text{MHz}$, $V_o = 400\text{V}$, $U_o = 25\text{V}$, $N^+$ can be trapped, $N_2^+$ and $N^{+2}$ can not be confined. (b) $N_2^+$ TOF spectrum at $\Omega = 1.2\text{MHz}$, $V_o = 400\text{V}$, $U_o = 25\text{V}$. 
RF (0.5 - 1.5 MHz) for trap's electrode

Synchronous trigger pulse in phase with rf waveform

10 Hz clock pulse from a LM555 oscillator

Laser flashlamp trigger signal

Single shot laser or electron gun trigger signal

Deflection plate gate signal

Dump signal synchronous with rf

Fig.(12) Timing diagram.
Fig. (13) Diagram of data acquisition and analysis system.
IV. EXPERIMENTAL METHOD AND PROCEDURE

1. Experimental Method and General Procedure.

Charge transfer rates are determined by measuring the relative number of ions remaining in the trap as a function of the time \( t \) after their production and of the pressure of the gas of interest. The charge transfer rate is dependent on the energy states of the multiply charged ions. After laser ablation, ions can be in various metastable states. For ions with sufficiently short metastable lifetimes, measurements can be made after they have decayed radiatively to their ground state. For those with longer lifetimes, a multi-exponential fit has to be used.

In a situation where the daughter ions are in the ground state, the resulting decay curve can be described by a simple exponential function

\[
N(t) = N_0 \exp(-t/\tau), \quad \text{with } 1/\tau = n<\sigma v> + n'<\sigma'v>
\]

where \( \tau \) is the decay constant. \( N_0 \) and \( N \) are number of stored ions at time zero and time \( t \), respectively. The \( n \) and \( n' \) are the particle densities of the neutral gas and the residual background gas. \( <\sigma v> \) and \( <\sigma'v> \) are the charge transfer rate coefficients for the ion and residual background of the vacuum system. \( \sigma \) is the charge transfer cross section, and \( v \) is the relative velocity between ions and neutral atoms. The decay constant \( \tau \) for each neutral gas can be extracted from the data by a least-squares fit to the time-dependent ion signals. Several decay constants \( \tau \) were obtained for different neutral-gas densities. The charge-transfer rate coefficient for the neutral gas is determined from the slope of the decay constant \( \tau \) vs \( n \) curves. The intercept gives the value of \( n'<\sigma'v> \), the charge transfer rate of multiply charged ions with the residual background gas. The values of \( n \) and \( n' \) can be accurately determined using a calibrated ion gauge and a residual gas analyser.

Several steps have to be carried out before the measurements can be made. First, we have to create enough Mo\(^{6+}\) ions. Second, we have to cool these energetic
laser induced ions and store them in the trap. And third, we have to select Mo$^{6+}$ ions in the trap since laser ablation creates Mo ions of other charge states. We shall discuss each step in some detail.

2. Ion Production By Laser Ablation And Ion Cooling

Laser ablation has been used previously to produce both neutral atoms and ions from solids.\(^{31-34}\) The number and charge states of ions produced by laser ablation depend on the laser energy and the laser power density. The number of ions produced per laser shot is large, about $10^{14}$ in the current investigation. It is difficult to trap multiply charged ions because the kinetic energy of these ions is high (tens to hundreds of eV) and the potential well of the trap is low (a few eV). In order to trap multiply charged ions from ablation plasmas, it is essential to decrease the kinetic energy of the ions. We cool these ions by collision. Two ion beams produced simultaneously by laser ablation cross at right angles inside the ion trap. A few ions in one beam undergo collisions with ions from the other beam. The result is that some of the ions lose almost all their kinetic energy and remain in the trap while others approximately double their energy and leave the trap. We can use simple elastic collision theory from classical mechanics to explain this cooling effect. Two billiard balls which have same mass $M$ and speeds $V_1$ and $V_2$ along exactly orthogonal trajectories approach one another from — infinity along the x and y axes. In a perfectly elastic collision, one ball remains at the origin with zero velocity, and the other moves away along a line in the $x$—$y$ plane with a speed $V_r = (V_1^2 + V_2^2)^{1/2}$ when the line joining the centers of the balls during collision is parallel to either one of the two initial trajectories. In the case of collisions of multiply charged ions from the crossed ablation beams, only a small number of ions remain in the trap. Since there are $10^{14}$ ions in each ablation pulse, a small fraction is still a very large number. In practice, the number of ions that can be
stored is limited to about $10^6$ because of space charge effects.

3. Ion Storage And Selection.

The charge states of ions produced by laser ablation is dependent on the power density of the ablation laser. After laser ablation, molybdenum ions can be in many different states. It is very important to exclude the ions other than Mo$^{6+}$ from storage. Specific groups of ions can be stored in the trap by judicious choice of the trapping parameters ($V_0$, $U_0$, $\Omega$). One can use the rf ion trap to select the ion of interest for study.

Close examination of the trapping parameters for Mo$^{q+}$ (where $5 \leq q \leq 7$) and the effect on the ion makeup of the signal is necessary. With the trap parameters set at $\Omega = .948$ MHz, $V_o = 345$ V, $U_o = 25.7$ V, the operating point of Mo$^{6+}$ is at $q_z = 0.6$, $a_z = -0.09$, and lies on the spherical potential well line (See Fig.(14a, b)). This will give the maximum stability for Mo$^{6+}$. But at these trapping parameters, Mo$^{5+}$ ($q_z = 0.5$, $a_z = -0.07$) and Mo$^{7+}$ ($q_z = 0.7$, $a_z = -0.10$) will also be confined (see Fig.(14a)). Due to the lower ionization energy of Mo$^{5+}$ (97 eV) compared to Mo$^{6+}$(158 eV), large quantities of Mo$^{5+}$ will be stored. The mass-to-charge ratios ($m/q$) of Mo$^{5+}$, Mo$^{6+}$, Mo$^{7+}$ are 19.3, 16, and 13.7 respectively. The mass resolution ($M/dM$) of our TOF spectrometer is about 5, which is not adequate to resolve these ions in the detection phase. With the trap parameter set at $\Omega = .948$ MHz, $V_o = 345$ V, $U_o = 44$ V, the operating point of Mo$^{5+}$ is out of the stable area and can not be trapped. Mo$^{6+}$ ($q_z = 0.6$, $a_z = -0.15$) and Mo$^{7+}$ ($q_z = 0.7$, $a_z = -0.17$) are inside a nonspherical well at the edge of the stable region, so they can be trapped (see Fig.(15a)).

We can exclude Mo$^{5+}$ from the trap after laser ablation by setting $U_o = 44$ V for about 5 ms putting Mo$^{5+}$ just out of the stable area. After the Mo$^{6+}$ (and probably a small quantity of Mo$^{7+}$) are stored, we immediately switch $U_o$ back to 25.7 V so that Mo$^{6+}$ is on the spherical well giving maximum stability. Just before the ions are
extracted from the trap for analysis, we switch $U_0$ to 44V for 5 ms to expel the Mo$^{5+}$ ions produced by the charge transfer of Ar and Mo$^{6+}$. This guarantees no Mo$^{5+}$ contamination in our Mo$^{6+}$ signal. A electronic switching circuit was constructed to satisfy this requirement. In this system, we could not shift the operating point to allow Mo$^{6+}$ to stay in the trap and Mo$^{7+}$ out of the trap. From Fig.(15b) we can see that Mo$^{6+}$ ($q_z = 0.6, a_z = -0.15$) lies in a more stable region than Mo$^{7+}$ ($q_z = 0.7, a_z = -0.17$), so more Mo$^{6+}$ ions should be confined than Mo$^{7+}$ ions. In addition, Mo$^{6+}$ is much easier to produce than Mo$^{7+}$, because the ionization energy needed for Mo$^{6+}$ (158 eV) is less than Mo$^{7+}$ (226 eV). Furthermore, Kwong (1989)$^{20}$ reported that no Mo$^{7+}$ had been stored in the trap using the same facilities. This observation is experimentally confirmed in current studies. It is reasonable to assume that contamination by Mo$^{7+}$ is negligible.

The ionization potentials of molybdenum and argon at different charge states lead one to suspect the following processes may be occurring:

\[
\begin{align*}
&Mo^{6+} + Ar \rightarrow Mo^{5+} + Ar^{1+} \\
&Mo^{6+} + Ar \rightarrow Mo^{4+} + Ar^{2+} \\
&Mo^{6+} + Ar \rightarrow Mo^{3+} + Ar^{3+} \\
&Mo^{6+} + Ar \rightarrow Mo^{2+} + Ar^{4+}
\end{align*}
\]

We have to determine contamination of ions of Ar$^+$, Ar$^{2+}$, Ar$^{3+}$ and Ar$^{4+}$ in our ion signal. The stability diagram (see Fig.(16a)) shows only Ar$^{3+}$($q_z = 0.71, a_z = -0.18$) and Ar$^{4+}$ ($q_z = 0.95, a_z = -0.24$) ions are in the stable area. The ion density of Ar$^{4+}$ could be ignored due to the unlikelihood of four electron charge transfer.

Using the following model, one can roughly estimate the influence of Ar$^{3+}$ on the decay constant of Mo$^{6+}$. The number of Mo$^{6+}$ ions at time $t$ is

\[
N_m = N_{0m} \exp(-t/\tau_m)
\]
Fig.(14) The operating points of Mo$^{5+}$, Mo$^{6+}$ and Mo$^{7+}$ in the stability diagram and the contour map. (a) Calculated results show that at $\Omega = 0.948$MHz, $V_o = 345$V, $U_o = 25.7$V Mo$^{6+}$ is on the spherical well, and Mo$^{5+}$, Mo$^{7+}$ can be trapped. (b) Contours represent the number of the ions trapped in the cylindrical trap (used in this experiment). From contour map, Mo$^{5+}$, Mo$^{6+}$ and Mo$^{7+}$ can be trapped.
Fig. (15) The operating points of Mo$^5+$, Mo$^6+$ and Mo$^7+$ in the stability diagram and the contour map. (a) Calculated results show that at $\Omega = 0.948$MHz, $V_o = 345$V, $U_o = 44$V Mo$^5+$ is out of the stable area, only Mo$^6+$ and Mo$^7+$ can be trapped. (b) From contour map, Mo$^5+$ can not be trapped, Mo$^6+$ and Mo$^7+$ can be trapped.
Fig. (16) The operating points of \( \text{Ar}^{3+} \) and \( \text{Ar}^{4+} \) in the stability diagram and the contour map. (a) Calculated results show that at \( \Omega = 0.948 \text{MHz}, V_o = 345 \text{V}, U_o = 44 \text{V} \), \( \text{Ar}^{3+} \) and \( \text{Ar}^{4+} \) can be trapped. (b) From contour map, \( \text{Ar}^{3+} \) can be trapped.
where $N_{om}$ is the number of Mo$^{6+}$ ions at zero time, $\tau_m$ is the decay constant of Mo$^{6+}$. At fixed pressure, $\tau_m$ is constant. Let us assume in the charge transfer of Mo$^{6+}$ with Ar that all argon ions produced are Ar$^{3+}$ ions. From the stability diagram (see Fig.(16b)), only 5% of the Ar$^{3+}$ ions produced by charge transfer can be stored in the trap at the region of $q_z = 0.71$, $a_z = -0.18$. The rate of change of Ar$^{3+}$ is given by the following differential equation,

$$\frac{dN_a}{dt} = \eta \frac{dN_m}{dt} - \frac{N_a}{\tau_a}$$

$$= \eta N_{om} \exp(-t/\tau_m) \frac{1}{\tau_m} - \frac{N_a}{\tau_a}$$

where $\eta = 5\%$ means that only five percent of Ar$^{3+}$ ions produced by charge transfer can remain in the trap. $\tau_a$ is the decay constant for the Ar$^{3+}$ charge transfer with Ar and residual gas. $-N_a/\tau_a$ is the number decrease rate of Ar$^{3+}$ due to the Ar$^{3+}$ charge transfer. If we assume the decrease rate of Ar$^{3+}$ due to charge transfer is small, then we can ignore $\frac{N_a}{\tau_a}$, and the equation becomes,

$$\frac{dN_a}{dt} = \eta N_{om} \exp(-t/\tau_m) \frac{1}{\tau_m}$$

$$N_a = \eta N_{om} [1 - \exp(-t/\tau_m)]$$

The total number of Mo$^{6+}$ and Ar$^{3+}$ ions is

$$N(t) = N_{om} \exp(-t/\tau_m) + N_a$$

The decay constant which has Ar$^{3+}$ contamination can be extracted from the data by a least-squares fit to the time-dependent ion signal. In Fig.(17), the solid line is the Mo$^{6+}$ decay curve. The dashed line is the decay curve which considers the Ar$^{3+}$ ion density. With a time of 3$t$ the slopes of the two lines, obtained from the least-square fit, are 3.25 and 3.43 respectively. Therefore the influence of the contamination of
Fig.(17) Ion signal vs time plot for the Mo\textsuperscript{6+} signal and the Mo\textsuperscript{6+} + Ar\textsuperscript{3+} signal. The solid line is the Mo\textsuperscript{6+} decay curve. The dashed line is the decay curve which considers the Ar\textsuperscript{3+} contamination. The slopes of two lines, obtained from the least-square fit are 3.25 and 3.43 respectively.
Ar$^{3+}$ on the decay constant of Mo$^{6+}$ is 5.5%. Because Ar$^+$ and Ar$^{2+}$ need less ionization energy, the probabilities of producing these ions in the real charge transfer processes should be much larger than that for Ar$^{3+}$ ions. The error of the measured Mo$^{6+}$ decay constant due to contamination of Ar$^{3+}$ on the Mo$^{6+}$ should be much less than 5.5%. A new quadrupole mass analysis system will be built to further confirm this result.

The storage time of the ions in the ion trap is crucial in the charge transfer measurement. The storage time of Mo$^{6+}$ in vacuum was determined by monitoring the decrease of the signal magnitude when the stored ions were driven out of the trap at progressively longer delay time. As shown in Figure 18, the characteristic storage time ($1/e$) of Mo$^{6+}$ is about 40 seconds. The storage time is limited by charge transfer and elastic collisions between the stored ions and the residual background gas.

4. Ion Detection.

A 2.6 µs, −70V negative bias pulse with a rise time of 0.2µs was applied to the end cap electrode of the trap facing the CEM, to extract the stored ions out of the trap and into the cathode region of the CEM. Ions are detected by the CEM operated in the linear range. To ensure the linear response of the CEM, the maximum output current from the CEM is kept at less than 10% of the CEM dc bias current. We used N$_2^+$ to check the linearity region of the CEM. We mapped the output current of the CEM by applying a variable dc bias voltage on the deflection plate controlling the number of ions reaching the detector. By plotting the CEM peak output current as the function of bias voltage, the linear region (lower than −1900v) is identified by the convergence of their slopes (see Fig.(19)), which shows the signal from CEM should be less than 10mV with 1K terminator. In practice, we kept the signal intensity below 5mV during the experiments.

In all the measurements, one of the deflection plates is grounded and the other
Fig. (18) The decay curve of Mo\(^{6+}\) signal vs time at residual gas pressure of 2x10\(^{-9}\) Torr in the vacuum chamber. The storage time of Mo\(^{6+}\) \(\tau = 39.5\) sec.
Fig.(19) The linear region of the CEM. $N_2^+$ signal normalized
at signal = 900mV, CEM voltage = 2500V.
plate is biased to +100V before the creation of ions. The purpose of added voltage to
the deflection plate is to prevent any stray ions from reaching the detector and
causing permanent damage when the laser or electron gun is on. The deflection plate
voltage has no effect on the charge transfer rate.

5. Pressure Calibration

In all the measurements, a Masstorr DX100 was used to determine the pressure
of the vacuum chamber. The filament of the Masstorr DX100 has different ionization
efficiencies for different gases, so the pressure read from it is not the real pressure of
the vacuum chamber. The particle density of neutral gas n used to determine the
charge transfer rate is directly proportional to the chamber pressure, so a careful density
calibration of the Masstorr DX100 is required. The relation between the pressure read
from Masstorr DX100 and the pressure in the chamber is

\[ P_{\text{chamber}} = \lambda P_{\text{DX100}} \]

where \( P_{\text{chamber}} \) is the pressure of the chamber and \( P_{\text{DX100}} \) is the pressure measured
by DX100, \( \lambda \) is constant for a particular gas.

Figure (20) is the diagram of the calibration apparatus. A 1 liter gas reservoir
was connected to the chamber through a leak valve (valve 2). A very thin copper disk
with a 1cm diameter hole in its center was installed to choke the diffusion pump inlet.
Assuming molecular flow, the pressure in the vacuum chamber is described by the
simple equation\(^{29}\)

\[ P_{\text{chamber}} = P_{\text{reservoir}} (C_{\text{leak valve}}/C_{\text{hole}}) + P_{\text{outgas}} \]

where \( P_{\text{reservoir}} \) and \( P_{\text{outgas}} \) are the reservoir pressure and pressure due to outgassing in
the chamber; \( C_{\text{leak}} \) and \( C_{\text{hole}} \) are the conductance of the leak valve and aperture plate
respectively. The conductance of the hole is calculated for molecular flow from the
relation\(^{30}\),

\[ C_{\text{hole}} = 3.7 \left( \frac{T}{M} \right)^{1/2} A \]
Fig. (20) Block diagram for pressure calibration.
where $T$ is the temperature of the gas, $M$ is the molecular mass of the gas, and $A$ is the area of the hole. The conductance of the leak valve is measured by reservoir pressure as a function of time. The reservoir pressure is measured by a Baratron-type 122A capacitance manometer (accuracy ± 0.05%). During calibration, valve 1 was opened to fill the reservoir with a particular gas. Valve 1 was then closed. The leak valve (2) was opened to let the gas into the vacuum chamber. Gas reservoir pressure was measured as a function of time. The equation modeling pressure change in the reservoir is

$$V \frac{dP}{dt} = -C_{\text{leak}}P$$

$$P(t) = P_0 \exp\left(-\frac{C}{V} t\right)$$

$$\ln P(t) = \ln P_0 - \frac{C}{V} t$$

where $V$ is the volume of the reservoir, $P$ is the pressure of reservoir.

In the calibration experiment, the pressure of the Baratron and of the Masstorr DX100 were monitored and simultaneously read. The conductance of the leak valve can be detected from the graph of $\ln P(t)$ vs $t$. Measurement of the background pressure with no gas load and the pump choked is $2 \times 10^{-9}$ Torr. This base pressure allows us to essentially neglect the outgassing term $P_{\text{out gas}}$ when calibrating the gauges in the $10^{-7}$ Torr region. The pressure of the vacuum chamber at different times was calculated, and the calculated pressure of the vacuum chamber vs the pressure reading of Masstorr DX100 was plotted. The slope of this straight line is the value of $\lambda$. For argon, the value of $\lambda$ is measured to be 0.443. The real pressure in the vacuum chamber is the pressure read from Masstorr DX100 times 0.443.
6. Data Analysis Procedure.

Twenty measurements of the Mo$^{6+}$ ion peak at a particular pressure were made for a specific delay time, and were stored in the computer's memory. The average intensity of the ion signals from twenty runs was obtained. The Sigmaplot software program was used for data fitting. The resulting ion decay constant, as well as uncertainties in the weighted least-square-fit are stored in the computer's hard disk for archival and future analysis. Measurements were made at different pressures to get a series of ion decay constants for the corresponding pressures.
V. EXPERIMENTAL RESULTS

Seven sets of measurements, taken at different Ar pressures ranging from $0.46 \times 10^{-7}$ Torr to $3.65 \times 10^{-7}$ Torr, were used to obtain the final results. Figure 21 is a plot of the ion signal intensity as a function of time for the seven experiment runs. The ion decay rate ($1/t$) at $0.46 \times 10^{-7}$ Torr was about 0.23 second$^{-1}$. After laser ablation, a substantial number of ions can be in various metastable states. For ions with sufficiently short lifetimes of these metastable states, measurements can be made after the ions have decayed to their ground state. The ion signal data are fitted with a single exponential decay curve to get the decay constant. The data points on each curve are the mean of twenty runs. The results of the fit are shown in the table I.

<table>
<thead>
<tr>
<th>Ar Pressure (Torr)</th>
<th>Decay Rate (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.46 \times 10^{-7}$</td>
<td>$0.23 \pm 0.02$</td>
</tr>
<tr>
<td>$0.90 \times 10^{-7}$</td>
<td>$0.29 \pm 0.03$</td>
</tr>
<tr>
<td>$1.35 \times 10^{-7}$</td>
<td>$0.51 \pm 0.04$</td>
</tr>
<tr>
<td>$1.80 \times 10^{-7}$</td>
<td>$0.51 \pm 0.06$</td>
</tr>
<tr>
<td>$2.43 \times 10^{-7}$</td>
<td>$0.79 \pm 0.05$</td>
</tr>
<tr>
<td>$2.93 \times 10^{-7}$</td>
<td>$1.05 \pm 0.14$</td>
</tr>
<tr>
<td>$3.65 \times 10^{-7}$</td>
<td>$1.43 \pm 0.14$</td>
</tr>
</tbody>
</table>

The characteristic decay rates are plotted as a function of Ar pressure (See Fig.(22). The ion density $n$ is directly proportional to pressure, $n = CP$. The slope of
Time Dependence of Stored Mo⁶⁺ Ions

Fig.(21) The decay curves of Mo⁶⁺ signal vs time under various Ar pressure.
Fig.(22) \( \text{Mo}^{6+} \) decay rate vs Ar pressure. The slope of this line gives charge transfer rate

\[
k = 1.02 \times 10^{-10} \text{ cm s}^{-1}
\]
this straight line, obtained from a weighted least-square fit to these seven points, is

\[
\tau = \frac{\Delta(1/\tau)}{\Delta(P)} = \frac{\Delta(1/\tau)}{\Delta(n/C)} = C - \frac{\Delta(1/\tau)}{\Delta(n)} = Ck
\]

where \( k \) is the rate coefficient. The value of \( C \) is \( 3.24 \times 10^9 \) atoms/Torr at room temperature. The charge transfer rate coefficient of Ar and Mo\(^{6+}\) is

\[ k = 1.02 \pm 0.10 \times 10^{-10} \text{ cm}^3\text{s}^{-1}. \]

As is seen in Fig. 22, the intercept at zero pressure is approximately zero indicating that charge transfer with unknown residual gases in the vacuum is negligible. The estimated uncertainty of the result is ± 10% and is mainly due to the accuracy of the Ar density measurements and the uncertainty in the statistical fluctuations of the ion signals.
REFERENCES

Appendix

Measurement of Ion Signal at Time T (Each signal is calculated from the average 20 measurements)

Ar Pressure: $0.46 \times 10^{-7}$ Torr

<table>
<thead>
<tr>
<th>Time (sec.)</th>
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</tr>
<tr>
<td>9.0</td>
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**Ar Pressure: 0.90 x 10^{-7} Torr**

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Ar Pressure: $1.35 \times 10^{-7}$ Torr

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Ar Pressure: $1.80 \times 10^{-7}$ Torr

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Ar Pressure: $2.43 \times 10^{-7}$ Torr

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Ar Pressure: $2.93 \times 10^{-7}$ Torr

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**Ar Pressure: 3.65 \times 10^{-7} \text{ Torr}**

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