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HIGH RESOLUTION ION KINETIC ENERGY ANALYSIS OF FIELD EMITTED IONS

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Abstract - Ion kinetic energy distributions in pulsed-laser stimulated field desorption of inert gases and deuterium, and in field evaporation of metal-helide ions have been obtained by using the high resolution pulsed-laser time-of-flight atom-probe. For field desorption of deuterium in a field of 2.0 V/Å to 3.0 V/Å, field induced resonance tunneling peaks and features of field dissociation process in D^+ and D_2^+ have been clearly observed. The energy distributions of D^+ contain a small primary peak which is due to formation of the ions in the ordinary field ionization zone. The secondary peaks, which may be more prominent than the primary peak, are ions formed in field dissociation of those D_2^+ ions produced in field ionization zone and also in resonance tunneling. As the resolution of the pulsed-laser ToF atom-probe has now been improved by a factor of at least 5, we are also searching for secondary structures produced by the vibrational motion in field dissociation of $HeRh^{2+}$ ions.

I. INTRODUCTION

The measurement of ion energy distributions provides direct information for understanding the mechanisms of ion formation in field ion emission,^{1,2} which includes field ionization, field desorption, field evaporation and field dissociation. The distribution width represents the width of the spatial zone where the ions are formed, and the critical energy deficit provides the energetics of ion formation.³ It is possible to study ion energy distributions using the high resolution pulsed-laser time-of-flight atom-probe, and a series of measurements has already been successfully carried out.^{4,5}

There are currently two interesting subjects for ion energy distribution studies of field desorbed ions. One is the field-induced resonance tunneling which was found by Jason et. al.⁶ in field ionization of hydrogen where a series of secondary peaks were found in the ion energy distributions of H^+ and H_2^+ . This phenomenon is explained in terms of resonance tunneling through field induced quantum states at the surface. These field induced "surface states" are formed in the "triangular potential well" of the applied field and the surface potential. The other subject is field dissociation of compound ions which was treated by Hiskes for H_2^+ and HD^+ as an atomic tunneling of H in 1961. Related experiments were reported for molecular ions H_2^+ and HD^+ ,⁸ and for metal-helide ions $HeRh^{2+}$.⁹ In a sufficiently high field, these ions will field dissociate within a short period of time following their formation in their respective field ionization zone. The dissociation products are an atomic ion and a neutral atom. The neutral atom may be field ionized again. These ions will have less kinetic energy than those formed directly in their field ionization zones. Thus by measuring ion energy distributions, these ions and even neutral particles can be identified.

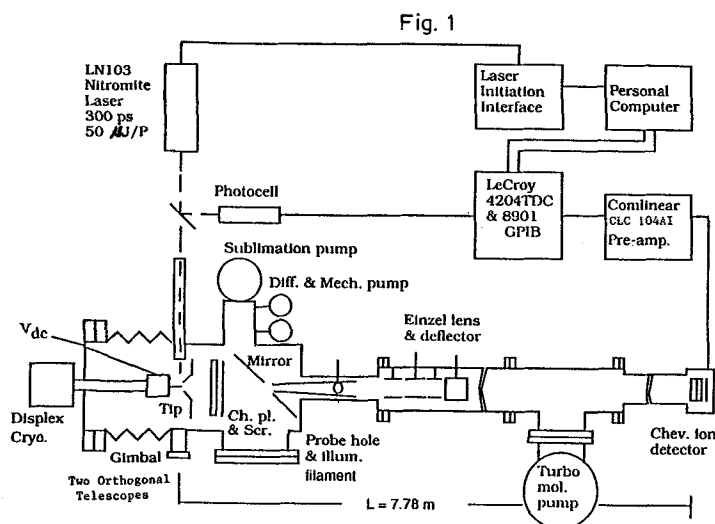
In a previous measurement of ion energy distributions in field ionization of H_2 and HD , it is found that a structure exists in the energy distribution of atomic ions H^+ which is significantly different from those in the energy distributions of H_2^+ and HD^+ . This is interpreted to indicate that H^+ ions are formed by field dissociation. We believe field desorption of deuterium is a good way to study both resonance tunneling and field dissociation for the following reasons. First the mass of the atoms involved are small enough for the atomic tunneling effect to be important. Second, we believe D_2 molecules are desorbed with an orientational coherence. As will be shown later, our energy distributions of D_2^+ and D^+ show clearly resonance tunneling peaks and secondary peaks due to field dissociation. As the resolution of our Pulsed-laser time-of-flight atom-probe has been improved by a factor of over 5, we are also searching for fine structures due to the vibrational motion of He and Rh^{2+} in field dissociation of $HeRh^{2+}$. Such structures, even if exist, would still be difficult to find even with the excellent resolution of the atom-probe before the recent new improvements.

II. INSTRUMENTATION AND EXPERIMENTAL PROCEDURES

The instrument used in this study is the high accuracy and high resolution pulsed-laser time-of-flight atom-probe field ion microscope. It has now been further improved with the installation of two LeCroy Model 4204 TDC of 156.25 ps time resolution and a 1.1 GHz band width preamplifier for the ion signal detection. The flight path has been lengthened to ~ 778 cm and a highly stable high voltage power supply of 2 parts in 10^6 per hour stability has been used for the tip voltage. Cares are also now exercised to maintain the room temperature constant to better than $\pm 1^\circ C$ so that the ion flight path will not change more than ± 1 part in 10^5 by thermal expansion of the flight tube. A schematic diagram of this system is shown in Fig. 1. With these and other precautions, an energy resolution of 1 part in 50000, or about 0.05 eV to 1 eV depending on the charge state of the ion species and the tip voltage, can now be achieved routinely. The flight times of ions are recorded in units of 156.25 ps, and are analyzed in histograms of bin width in integral multiples of 156.25 ps.

The onset flight time t_0 , i.e. the flight time of the most energetic ions, of an ion species of charge ne is related to the tip voltage V_0 , the mass-to-charge ratio M/n , and the critical ion energy deficit ΔE_c^{n+} by⁵

$$M/n = C[V_0 - \Delta E_c^{n+}/ne](t + \delta)^2, \quad (1)$$



where ΔE_c^{n+} is given by

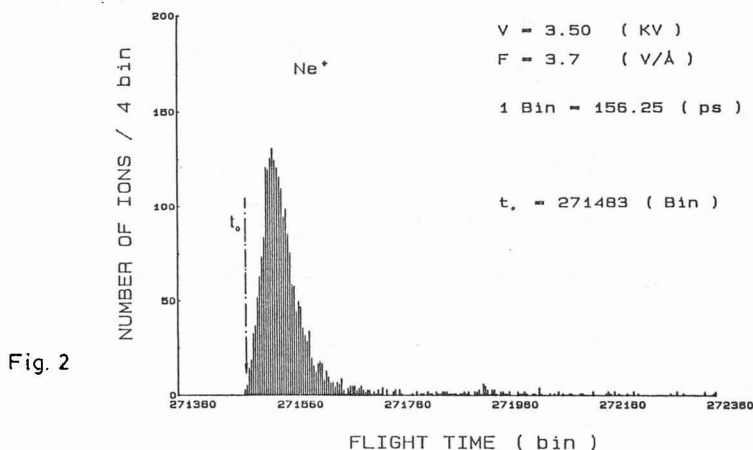
$$\Delta E_c^{n+} = \Lambda + \sum_i n I_i - n \phi_{av} - Q, \quad (2)$$

where Λ is the binding energy of the atoms on the surface, I_i is the i th ionization energy of the atoms, and ϕ_{av} is the average work function of the flight tube wall, and Q is the activation energy which is omitted in data analysis. This equation is derived from consideration of a Born-Harber energy cycle, thus intermediate effects of electric field are eliminated. C and δ are the flight path constant and the time delay constant of the system. They can be very accurately determined from the onset flight times of pulsed-laser field desorbed inert gas ions using a precision calibration method.⁵ We have carried out this calibration for our system after the improvements, and the present values are $C = 0.003188792 \text{ u}/\mu\text{s}^2/\text{kV}$ and $\delta = 7.68 \text{ ns}$. It is now possible to determine routinely ion masses and kinetic energies with an accuracy of 1 to 2 parts in 10^5 .

An ion energy distribution obtained is shown in Fig. 2 for pulsed-laser field desorbed Ne from a field evaporated tungsten surface. The tip was cooled down to 40 K and the laser intensity was kept very low, just sufficient to desorb field adsorbed atoms. The Ne gas pressure was 8×10^{-8} Torr. This energy distribution, taken at a field slightly higher than the best image field, has a full width at half maximum (FWHM) of 1.44 eV, and the onset flight time is 42420 ns (or 271488 bins) which corresponds to a critical energy deficit of 17.195 eV. This experimental value differs only by 0.76 % from the theoretical value of 17.064 eV. If we use the theoretical critical energy deficit to calculate the ion mass, a value to 19.992645 u is obtained which differs from a standard table value by 0.000755 u.

III. RESULT AND DISCUSSIONS

Our measurements were done at a tip temperature of $\sim 40 \text{ K}$ and the background vacuum was in 1.5×10^{-9} to middle 10^{-10} Torr range. We have investigated the pulsed-laser field desorption of deuterium from the lattice steps of the tungsten (110) plane at a field near or above the best image field which is $\sim 2.2 \text{ V}/\text{\AA}$. The gas pressure was kept around 1×10^{-7} Torr. A few of the kinetic energy distributions obtained are shown in Fig. 3 and Fig. 4. A laser pulse heats the surface for a very brief period of time to cause thermal desorption of field adsorbed deuterium gas molecules. When they pass through the ionization-zone, a fraction of them will be field ionized. The flight time distribution of D_2^+ shown in Fig. 3, which is also the ion kinetic energy distribution, shows clearly resonance tunneling peaks in the field of about $2.2 \text{ V}/\text{\AA}$. From these well defined peaks in the ion energy distributions, the energies of the field induced surface quantum states under various fields are derived, and they are listed in Table 1. The energy distribution of D^+ , shown in Fig. 4, is a little more complex and is also very interesting. The onset flight time of the primary peak, which appears smaller than the secondary peaks, agrees



with that expected for D^+ ions in field ionization. Thus these ions are produced right in the ionization zone of atomic deuterium. The second peak is from D^+ ions produced by field dissociation of molecular D_2^+ ions. It has a larger energy deficit for the following two reasons. 1). The critical energy deficit in field desorption, which is the same as in field ionization, of D_2^+ is larger than D^+ by $10.968 - 9.098 = 1.87$ eV. 2). The additional energy loss of D^+ during the process of field dissociation of D_2^+ is about 3.0 eV according to a theoretical calculation.⁸ Thus the energy difference in the first

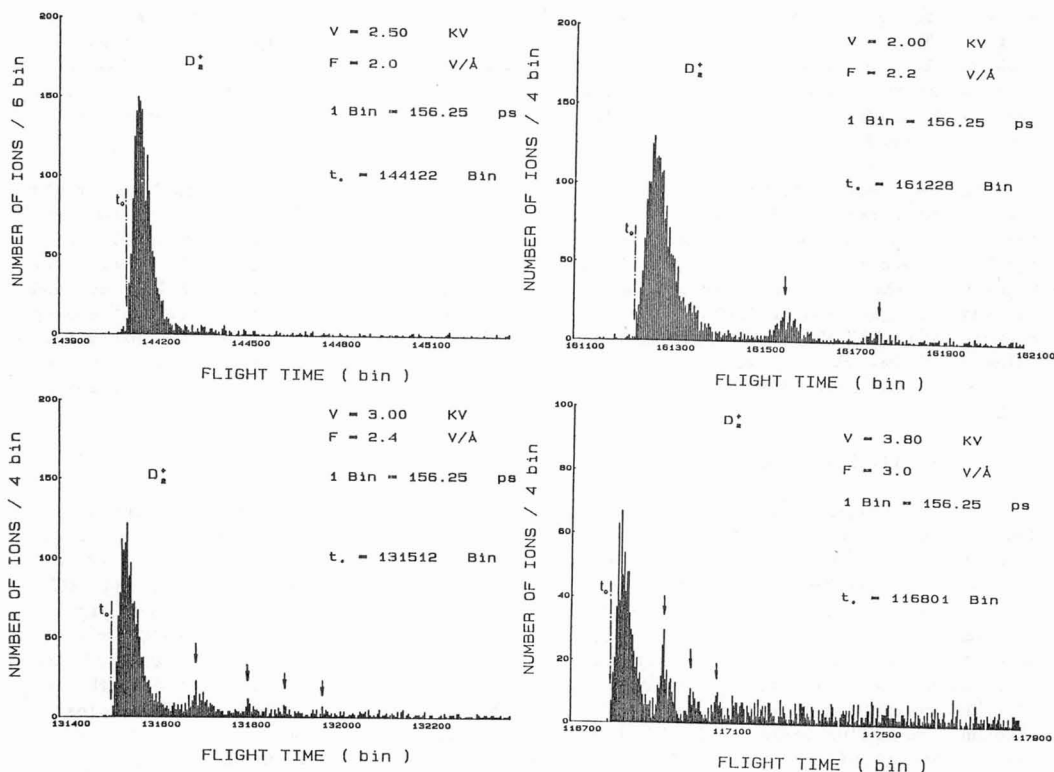


Fig. 3

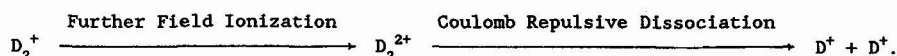
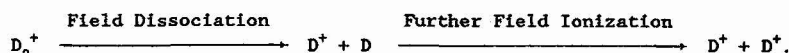
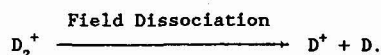
two peaks of the D^+ ion energy spectrum should be 4.87 eV. Our measured values are 4.90 eV at 2.2 V/Å and 4.91 eV at 2.4 V/Å, in excellent agreement with the calculation. In our experiment, the energy difference between two peaks can be easily obtained by

$$\Delta E/E \approx \Delta E/neV_0 \approx 2\Delta t/t. \quad (3)$$

Table 1. Energy Difference from the Main Peak in D_2^+

Field V/Å	Main Peak eV	2nd Peak eV	3rd Peak eV	4th Peak eV	5th Peak eV
2.0	0.0				
2.2	0.0	7.24	12.30		
2.4	0.0	7.30	12.22	15.87	
3.0	0.0	7.54	12.23	16.91	20.30

The dissociation should be one of the following processes:



The last two processes will produce a low energy tail in the energy distribution of D^+ since both the further field ionization and Coulomb repulsive dissociation take time.

In the energy distribution of D^+ , there are usually a few secondary peaks. Table 2 lists the energy separations of these secondary peaks with the primary peak, which is in fact smaller than most of the secondary peaks. By comparing with Table 1, we conclude that these secondary peaks contain field dissociated D^+ ions from those D_2^+ ions formed in the resonance tunneling process. In a low field of about 2.0 V/Å, the resonance peaks in D_2^+ are almost nonexistent, so are the secondary peaks in the energy distribution of D^+ ions. At a very high field, about 3.0 V/Å, almost 90% of all the D_2^+ ions will be field dissociated, and thus D^+ ions give a large energy spread in the energy distribution with the secondary peaks clearly visible.

Table 2. Energy Difference from the First Peak in D^+

Field V/Å	First Peak eV	2nd Peak eV	3rd Peak eV	4th Peak eV	5th Peak eV
2.0	0.0				
2.2	0.0	7.18	11.54		
2.4	0.0	7.22	11.87		

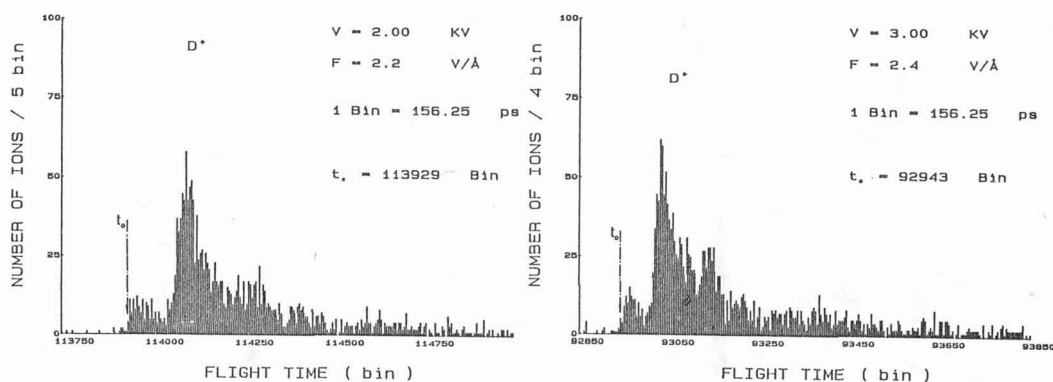


Fig. 4

Field dissociation of HeRh^{2+} is very different from that of D_2^+ . HeRh^{2+} can only be formed right at the surface whereas D_2^+ can be formed very far away from the surface as those D_2^+ ions in the resonance tunneling peaks. At the instant of field desorption, the axis of HeRh^{2+} is antiparallel to the direction of the field, thus it cannot be field dissociated. It has to rotate by at least 90° for the field dissociation to be possible. Maximum dissociation rate occurs when it is rotated by 180° from the as desorbed orientation. It is expected that field dissociation rate also depends on the vibrational phase angle of He and Rh^{2+} , maximum when these two particles are moving away from each other in their vibrational motion. We should be able to detect vibrational features in the secondary peak of Rh^{2+} in field dissociation of HeRh^{2+} . We have been searching for these features and Fig. 5 shows a preliminary result of the energy distributions of Rh^{2+} and HeRh^{2+} . Unfortunately the amount of data we have collected so far is still too small, and even though there is indication of such features, it is still uncertain. We are presently continuing this search.

IV. SUMMARY

We have studied the ion kinetic energy distributions in field ion emission with the high resolution pulsed-laser time-of-flight atom-probe. Good quality kinetic energy distributions of D_2^+ , D^+ in field desorption of deuterium, and of HeRh^{2+} and Rh^{2+} in field evaporation of Rh in He, showing features of resonance tunneling and field dissociation effects, have been obtained.

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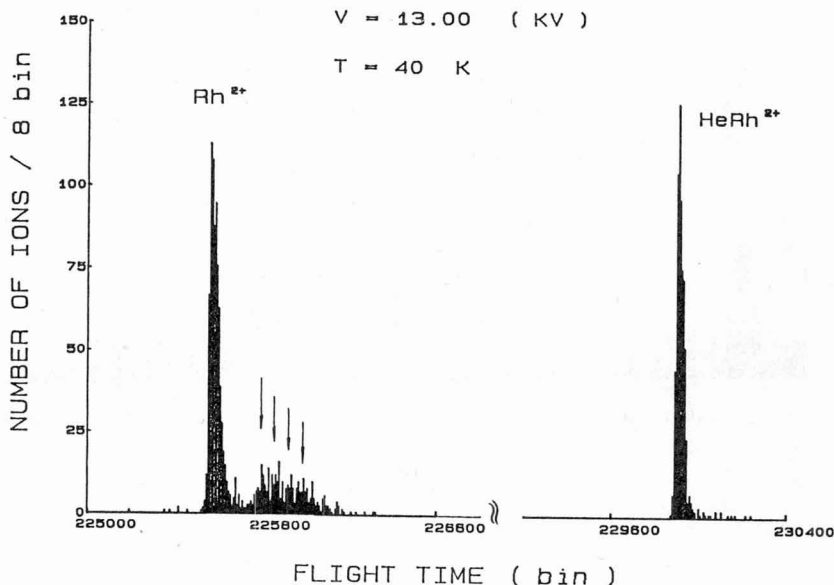


Fig. 5