

Time-of-Flight Energy and Mass Analysis of Metal-Helide Ions and Their Formation and Dissociation

T. T. Tsong and Y. Liou

Physics Department, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 19 March 1985)

An ion reaction-time amplification scheme is used to study field dissociation of RhHe^{2+} formed by low-temperature field evaporation of Rh in He. Field dissociation of RhHe^{2+} can occur by atomic tunneling within a few times 10^{-13} s in a well-defined spatial zone of width ~ 150 Å above the emitter surface. The time resolution of this measurement is as good as 20 fs.

PACS numbers: 68.45.Da, 79.70.+q, 82.65.Nz, 82.80.Ms

In low-temperature field evaporation of metals in helium of pressure greater than 1×10^{-8} Torr, metal-helide ions can be formed.¹ For Pt and W, metal-dihelide ions have also been observed.² No study of the stability of metal-helide ions has been reported. We report here an observation of dissociation of RhHe^{2+} ions. This dissociation occurs in less than a few times 10^{-13} s in a well-defined spatial zone of width ~ 150 Å which is centered around 220 Å above the emitter surface. It can occur only in an applied field of ~ 4.8 V/Å, and thus it is experimental evidence of field dissociation of an ion as a quantum-mechanical tunneling phenomenon of atoms discussed theoretically by Hiskes.³ To study such a fast ion reaction, we have devised an ion reaction-time amplifica-

tion scheme to achieve a time resolution of 20 fs in our ion reaction-time measurement.

The instrument used in this study is a pulsed-laser time-of-flight atom-probe field-ion microscope⁴ shown in Fig. 1. This system, when carefully operated,⁵ can achieve an accuracy and resolution of better than 5 parts in 10^5 , i.e., 0.0005 to 0.005 u for low to heavy ions in mass measurements and 0.3 to 1.0 eV out of 6 to 20 keV in ion energy measurements. In ordinary time-of-flight spectrometers, the time resolution in ion reaction-time measurements is the overall time resolution of the time-measuring devices used in the systems. The laser pulses used in our atom probe are 0.3 ns in width, and the electronic timers used for the ion counting have a resolution of 1 ns. Thus the overall

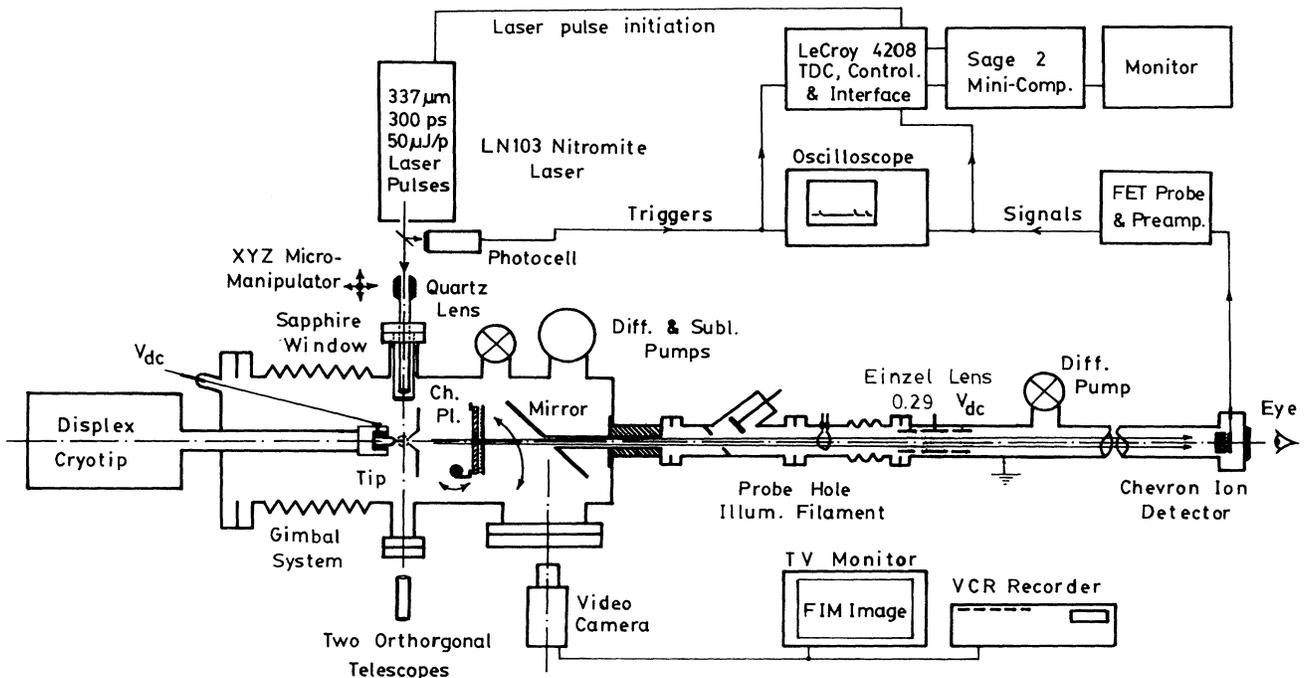


FIG. 1. The pulsed-laser time-of-flight atom-probe field-ion microscope. With an acceleration section of 1.5 mm and a free-flight path of 4200 mm, a resolution of 10^{-13} s can be achieved for measuring reaction times even though the time resolution of the system is only 1 ns. This capability may be called a reaction-time amplification.

TABLE I. Critical energy deficits, $\Delta E_c^{n+}/n$, for Rh and Pt and their helide ions.

	Expt.	Theory		Expt.	Theory
Rh ²⁺	10.7 ± 0.8 eV	10.9 eV	Pt ²⁺	11.1 ± 0.6 eV	11.4 eV
RhHe ²⁺	10.9 ± 0.4 eV	...	PtHe ²⁺	12.3 ± 0.5 eV	...

time resolution of the system is $\sim (0.3^2 + 1^2)^{1/2} \simeq 1$ ns, which is a few orders too slow to study field dissociation. To overcome this limitation we have devised an ion reaction-time amplification scheme to improve greatly the time resolution for measuring ion reaction times. Details of this scheme and its potential application cannot be described in this Letter and will be presented elsewhere.⁶ With this scheme those ion reaction events taking place in a very short time period can have their detection stretched over a much longer period. This is done by separating the system into two well-isolated sections, an ion acceleration-reaction section of length l and a field-free flight section of length L with $L \gg l$. The total flight time of an ion is then determined essentially by the final energy of the ion when it leaves the acceleration section. The final kinetic energy is, however, determined by the location in the acceleration section where the ion is formed. Therefore, the energy distribution of the daughter ion maps out the spatial distribution of the ion reaction events. The ion reaction rate is then determined from the velocity of the parent ions at the moment they are dissociated. In our system, we make $l \simeq 1.2$ mm and $L \simeq 4200$ mm. Detailed calculations using a parabolic configuration of the tip surface and the grounded electrode show that a time resolution of 10 to 20 fs can be achieved in the measurement of ion reaction times for our system.⁶ This corresponds to an amplification factor greater than 5×10^4 . Also with our system the spatial zone of ion formation can be determined to an accuracy of 0.06 to 0.2 Å.

It has already been established that metal-helide ions can be observed⁷ only if the emitter temperature is less than 100 K where field adsorption of helium on the emitter surface can occur⁸; thus metal-helide ions are not formed by collision between metal ions and gas atoms but by direct field evaporation from the emitter surface. This conclusion can be best established from a measurement of the critical energy deficit of helide ions and metal ions. Results for Rh²⁺ and Pt²⁺ and RhHe²⁺ and PtHe²⁺ are shown in Table I. The fact that metal-helide ions and metal ions have almost identical critical energy deficits clearly indicates that helide ions are formed right at the emitter surface as are the metal ions. Another interesting observation is that all the metals known to have the dc evaporation field greater than 4.5 V/Å form metal-helide ions of certain charge states as can be seen in Table II. No

metal-helide ions are observed for all those metals with their dc evaporation fields lower than 4.5 V/Å.

A high electric field can also induce field dissociation of these ions.³ In Figs. 2(a) and 2(b), ion energy distributions in pulsed-laser field evaporation of Rh are shown. When Rh is field evaporated in vacuum below 1×10^{-9} Torr, a very well-defined ion energy distribution as shown in Fig. 2(a) is obtained. There is no low-energy tail or noise signal in the entire spectrum. In a histogram, the true FWHM is the measured FWHM minus one to two bins. Our best data available (not shown), taken at 7.8 kV and $F_0 \approx 4.7$ V/Å, give $2.5 \text{ eV} < \text{FWHM} < 5 \text{ eV}$ for Rh²⁺ ions. This corresponds to an ionization zone of width of about 0.4 Å. This is probably still widened by the limited instrument resolution since as the resolution of our system improves, the width narrows. The true width is probably only about 0.2 to 0.3 Å as in field ionization.⁹ When Rh is field evaporated in $(1 \text{ to } 2) \times 10^{-8}$ Torr of He, a mass spectrum shown in Fig. 2(b) is obtained. Beside the RhHe²⁺ mass line, we find that now the Rh²⁺ line has a well-separated secondary peak about 30 ns behind the main peak. The energy distributions of RhHe²⁺ as well as the main peak of Rh²⁺ are still as sharp as the Rh²⁺ line obtained by field evaporation in vacuum. The secondary peak of Rh²⁺, in fact, is as prominent as the main peak when the Rh emitter is just being pulsed-laser field evaporated at a field only a few percent below the dc evaporation field. In this field range, 70% to 80% of field-evaporated ions are in the form of RhHe²⁺ ions, as indicated by the shaded parts of the mass

TABLE II. Ion species observed in low-temperature field evaporation in helium.

Element	Ion species	dc evaporation field (V/Å)
Mo	Mo ²⁺ , Mo ³⁺ , MoHe ³⁺	~ 4.8
Rh	Rh ⁺ , Rh ²⁺ , RhHe ²⁺	~ 5.0
Ta	Ta ²⁺ , Ta ³⁺ , TaHe ³⁺	~ 4.8
W	W ²⁺ , W ³⁺ , W ⁴⁺ , WHe ³⁺ , WHe ₂ ³⁺	~ 5.7
Re	Re ⁺ , Re ²⁺ , Re ³⁺ , ReHe ³⁺	~ 5.0
Ir	Ir ²⁺ , Ir ³⁺ , IrHe ²⁺	~ 5.3
Pt	Pt ²⁺ , PtHe ²⁺ , PtHe ₂ ²⁺	~ 4.6

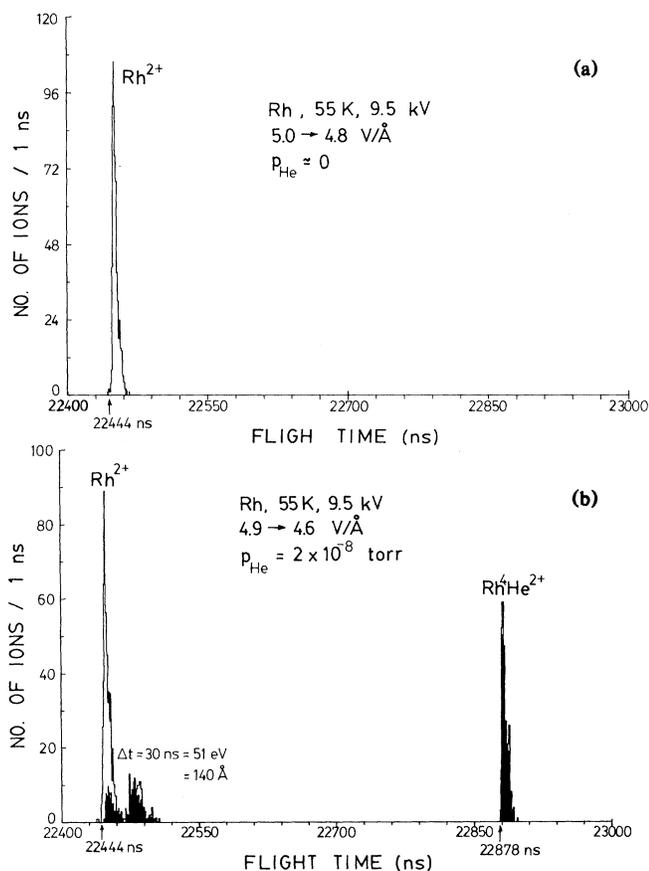
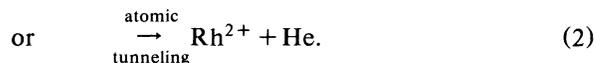
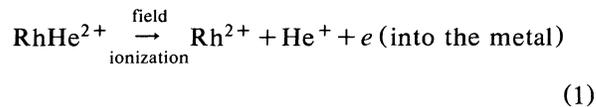


FIG. 2. (a) A pulsed-laser atom-probe mass spectrum of Rh taken in vacuum at 9.5 kV. Only Rh^{2+} ions are observed (b) In $(1 \text{ to } 2) \times 10^{-8}$ Torr of helium, in addition to the Rh^{2+} mass lines, a RhHe^{2+} mass line and a secondary peak in the mass line of Rh^{2+} appear.

lines. As the field at the emitter surface reduces by gradual field evaporation, the number of RhHe^{2+} ions decreases drastically, and so does the secondary Rh^{2+} peak. Thus there is no question that the secondary Rh^{2+} peak is indeed associated with the formation of RhHe^{2+} ions. Since the secondary peak indicates an additional energy deficit of 51 eV of the Rh^{2+} ions, these ions can only be formed at some distance away from the emitter surface. They can only be formed by field dissociation since a RhHe^{2+} ion, once formed, has no chance of interacting with another particle.

Two questions remain to be answered. The first question is whether the dissociation is spontaneous, and occurs at a constant dissociation rate. Our analysis⁶ shows that such a dissociation process will produce an exponentially decaying low-energy tail in the energy distribution of Rh^{2+} instead of the well-defined secondary peak we have observed. The well-defined secondary peak indicates that the dissociation

occurs within a narrow spatial zone of width w at a distance x from the metal surface where x and w can be estimated by considering the following dissociation reactions:



In either case, a detailed analysis⁶ will show that

$$x = \frac{1}{2} r_0 \{ \exp[4k(1 + M/m)\Delta t/t_0] - 1 \}, \quad (3)$$

where M and m are respectively the mass of Rh and He, r_0 is the tip radius, $k \approx 5$, and t_0 is the onset flight time of Rh^{2+} . Substituting the experimental values shown in Fig. 2(b) into Eq. (3) we find $x \approx 220 \text{ \AA}$ and $w \approx 150 \text{ \AA}$. It can be shown that it takes only $7.9 \times 10^{-13} \text{ s}$ for a RhHe^{2+} ion to travel from zero velocity a distance of 220 \AA near the emitter surface. We conclude that a fraction of RhHe^{2+} is dissociated in 4×10^{-13} to $1.2 \times 10^{-12} \text{ s}$. Once RhHe^{2+} ions are out of this "dissociation zone," they are completely stable.

The next question is which of the mechanisms, Eq. (1) or Eq. (2), is the correct one. Equation (1) is highly unlikely since field ionization usually occurs in a zone of width less than 0.5 \AA just beyond the critical distance of field ionization.⁹ Also Eq. (1) would predict the presence of a secondary peak in the energy distribution of pulsed-laser field desorbed He^+ ions which should be separated from the main peak by $\sim 600 \text{ eV}$. No such peak is observed. Equation (2) would predict emission of neutral He atoms of less than 50-eV kinetic energy which cannot be detected in our system. Since a RhHe^{2+} ion, once formed, has no chance of colliding with another particle, only two mechanisms of dissociation can satisfy the conservation of energy requirement. First, the dissociation may be induced by electronic deexcitation followed by vibrational excitation if pulsed-laser field desorption also involves electronic excitations by the laser pulses. However, the time constant in electronic deexcitation is in the 10^9 - 10^{-8} -s range, and it is spontaneous. Our observed dissociation time is less than 10^{-12} s . We must conclude that the dissociation is produced by tunneling of the He atom through a potential barrier which bound the two atoms together. This potential barrier is deformed by the electric field near the surface. Once a RhHe^{2+} is far away from the surface, the field is too low to have a sufficient deformation of the potential barrier, and no atomic tunneling becomes possible; thus RhHe^{2+} becomes stable.

Field dissociation as a tunneling phenomenon of

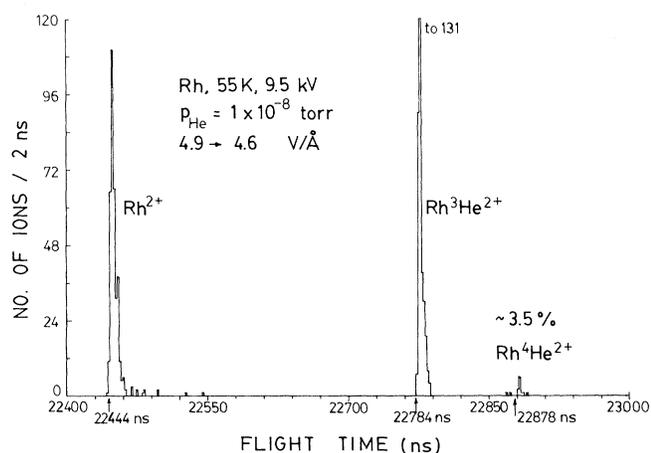


FIG. 3. Data taken under identical conditions except that ^4He gas is replaced with ^3He -3% ^4He gas.

atoms is very sensitive to the mass of the atoms and the effective potential barrier which is also mass dependent.³ A dramatic isotope effect is found when ^4He is replaced with ^3He as shown in Fig. 3. We do not have a satisfactory explanation yet but this should be of great interest to quantum theorists.

In summary, field dissociation of compound ions as a quantum-mechanical tunneling phenomenon of atoms,³ similar to field ionization as a quantum-mechanical tunneling phenomenon of atomic electrons,¹⁰ has been established for RhHe^{2+} . This field dissociation occurs in a very well-defined spatial zone, also similar to field ionization above a metal surface. This very fast ion reaction with a time constant in the 10^{-13} -s range can be studied in the pulsed-laser atom

probe by using a new ion reaction-time amplification scheme to achieve a time resolution of 20 fs.⁶ The same scheme can be adopted to other time-of-flight spectrometers to study fast ion reactions such as photodissociation, dissociation of cluster ions by electronic deexcitation-induced vibrational excitation or by field dissociation, dissociation time of multiply charged ions in Coulomb explosion, etc. As for ion reactions by atomic tunneling, any compound ions containing a light atom such as H, D, T, or He can be studied.

This work was supported by National Science Foundation Grant No. DMR-8217119.

¹E. W. Müller, S. B. McLane, and J. A. Panitz, *Surf. Sci.* **17**, 430 (1969); E. W. Müller and T. T. Tsong, *Prog. Surf. Sci.* **4**, 1 (1973).

²T. T. Tsong and T. J. Kinkus, *Phys. Rev. B* **29**, 529 (1984); T. T. Tsong, *Phys. Rev. B* **30**, 4946 (1984).

³J. R. Hiskes, *Phys. Rev.* **122**, 1207 (1961).

⁴T. T. Tsong, S. B. McLane, and T. J. Kinkus, *Rev. Sci. Instrum.* **53**, 1442 (1982).

⁵T. T. Tsong, Y. Liou, and S. B. McLane, *Rev. Sci. Instrum.* **55**, 1246 (1984).

⁶T. T. Tsong, to be published.

⁷E. W. Müller and S. V. Krishnaswamy, *Phys. Rev. Lett.* **31**, 1282 (1973).

⁸T. T. Tsong and E. W. Müller, *Phys. Rev. Lett.* **25**, 911 (1970), and *J. Chem. Phys.* **55**, 2884 (1971).

⁹T. T. Tsong and E. W. Müller, *J. Chem. Phys.* **41**, 3274 (1964); G. R. Hanson and M. G. Inghram, *Surf. Sci.* **55**, 29 (1976).

¹⁰J. R. Oppenheimer, *Phys. Rev.* **31**, 67 (1928).