Orientational and Isotope Effects in Field Dissociation by Atomic Tunneling of Compound Ions

T. T. Tsong

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

A strong isotope effect has been found in field dissociation by atomic tunneling of $HeRh^{2+}$, which can be reasonably well accounted for with a WKB calculation. Field dissociation can occur only if the ion is rotated by 180° from its desorbed orientation to line up properly with the field. This rotation time of a $^4HeRh^{2+}$ ion in a field of ~ 4.5 V/Å is determined to be 8×10^{-13} s.

Dissociation of compound ions in a high electric field was treated by Hiskes as an atomic-tunneling phenomenon,[1] similar to field ionization of an atom in a high electric field by tunneling of an atomic electron, first treated by Oppenheimer.[2] Evidence of field dissociation was based on an observation of H^+ when a beam of H_2 was passed through a region with a field greater than 10^5 V/cm.[3] Hiskes's calculations showed that such a field is needed to field dissociate H_2 at an observable rate. Recently Tsong and Liou reported clear evidence of field dissociation of $^4HeRh^{2+}$ in a field of ~ 4.5 V/Å based on a high-resolution time-of-flight ion mass and energy analysis.[4] I report here the observation of a dramatic isotope effect when ^4He is replaced with ^3He.

In some respects field dissociation of $^4HeRh^{2+}$ is similar to α decay which also occurs by a tunneling effect. A WKB calculation gives a reasonably good account of the isotope effect that we have observed. A theoretical model can explain why a fraction of $^4HeRh^{2+}$ ions are field dissociated within a time of 8×10^{-13} s of their formation, and also only in a narrow spatial zone. The resolutions of our time and spatial measurements are ~ 20 fs and ~ 0.3 Å, respectively.

$^4HeRh^{2+}$ can be produced by low-temperature (<100 K) field evaporation of a Rh tip in He of 1×10^{-8} Torr or higher, and in a field between ~ 4.5 and 5.0 V/Å. Under this field each surface Rh atom in the more protruding position undergoes field adsorption with a He atom. When the field evaporation is done with a weak stimulation (heat effect) of laser pulses of 300 ps width, a flight-time spectrum of ions such as shown in Figs. 1(a) and 1(b) is obtained. It contains a He^+ line, a Rh^{2+} line with a double-peak structure, and a $HeRh^{2+}$ line. The He^+ line and the main Rh^{2+} peak are identical to those of pulsed-laser-field-desorbed He^+ without field evaporation and of Rh^{2+} produced by field evaporation in vacuum.[4]

A flight-time difference of 30 ns of Rh^{2+} in the main peak and in the secondary peak [Fig. 1(b)] corresponds to an energy difference of 51 eV. With use of the field distribution of a parabolic electrode config-

uration one finds that Rh^{2+} in the secondary peak is formed in a spatial zone of ~ 150 Å width which is centered at ~ 220 Å above the emitter surface (Fig. 2). If $HeRh^{2+}$ dissociates by further field ionization followed by Coulomb dissociation into a He^+ and a Rh^{2+}, then the He^+ ions will have an energy ~ 600 eV less than those in the main peak and should show up at the flight time indicated by the arrow in Fig.
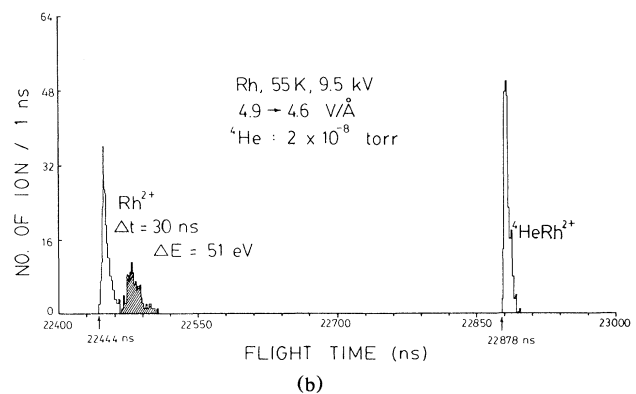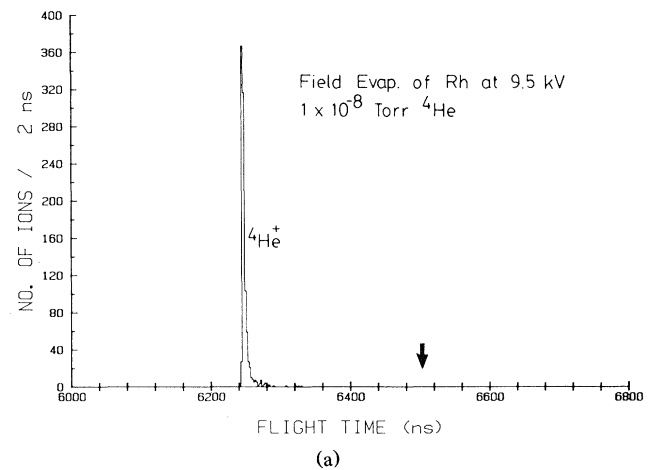

FIG. 1. (a) A section of the time-of-flight spectrum showing the energy distribution of He^+. (b) Another section showing the mass lines of Rh^{2+} and $^4HeRh^{2+}$.

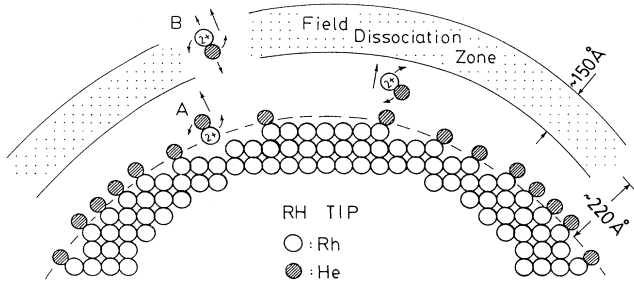FIG. 2. Schematic diagram showing the field-dissociation zone of $^4HeRh^{2+}$.

FIG. 3. The section of the time-of-flight spectrum showing Rh^{2+} and $^3HeRh^{2+}$.

1(a). No such peak indicates that $HeRh^{2+}$ dissociates into a He and a Rh^{2+}. The neutral He will acquire only 51 eV and cannot be detected in our system.

$HeRh^{2+}$ field dissociates in a well-defined spatial zone for the following reason. The relative motion of He and Rh^{2+} in a $HeRh^{2+}$ ion in a field F is governed by[1]

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}_n) + \left[U(\mathbf{r}_n) - \frac{2eFz_n}{(1+M/m)}\right]\psi(\mathbf{r}_n)$$
$$= E\psi(\mathbf{r}_n), \quad (1)$$

where $\mathbf{r}_n$ is a vector pointing from the He to the Rh^{2+}, μ is the reduced mass, z_n is the component of $\mathbf{r}_n$ along F, and $U(\mathbf{r}_n)$ is the interparticle potential. Field dissociation can occur only if z_n is positive. When a $HeRh^{2+}$ ion has just field evaporated it has the wrong orientation as shown by A of Fig. 2. As the ion is accelerated away it also rotates. As it rotates by 180° to orientation B it can dissociate. If it is not dissociated it has to wait for an additional rotation of 360°. By this time the ion is ~ 1100 Å away from the surface and the field is too low to cause field dissociation. Thus "8×10^{-13} s" is the time for the ion to rotate 180°. With use of a semiclassical estimate, this time is given by

$$t_j = \frac{\pi}{\omega_j} = \frac{\pi \mu r_n^2}{[j(j+1)\hbar]^{1/2}} \approx \frac{\pi \mu r_n^2}{j\hbar} \quad (2)$$

for large j, where ω_j is the angular speed when the rotational quantum number is j. Taking $r_n = 2.6$ Å and $\mu = 6.39 \times 10^{-27}$ kg, one finds that $t_{16} = 8 \times 10^{-13}$ s. This agrees best with our measured time. This state has maximum population at 510 K. The tip temperature was 55 K but laser pulses heated the surface to ~ 200 K for a few nanoseconds. The ion temperature thus seems to be much higher than the surface temperature. This calculation, however, does not account for the torque of the applied field. The angular acceleration time and the question of how the value of j increases as a result of the applied electric torque are
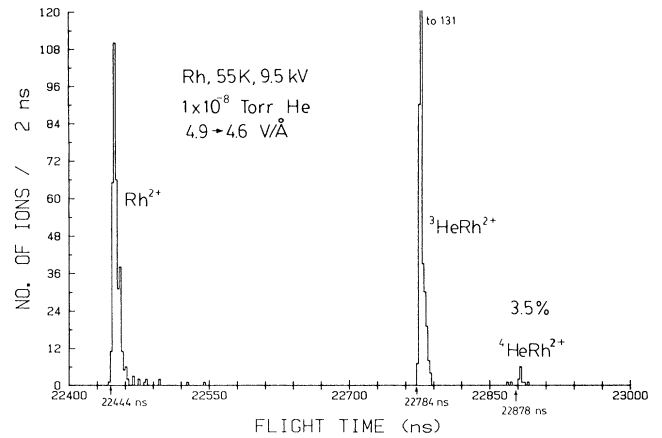
fundamental problems which should be of interest to quantum theorists.

When ^4He is replaced with ^3He, the secondary Rh^{2+} peak disappears as shown in Fig. 3. This dramatic isotope effect is due to the potential-barrier–reduction term, $-2eFz_n/(1+M/m)$; its magnitude is greatly reduced by the replacement of ^4He with ^3He. When $\mathbf{r}_n \parallel F$, the potential barrier of $HeRh^{2+}$ is shown in Fig. 4. If one approximates the segment of $U(\mathbf{r}_n)$ beyond r_n by a straight line of slope s_1, then the WKB barrier-penetration probability is given by[5]

$$D(h,F) = \exp\left[-\frac{4}{3}\left(\frac{2\mu}{\hbar^2}\right)^{1/2}\left\{\frac{1}{s_1} + \frac{1+M/m}{2eF}\right\}h^{3/2}\right],$$
$$(3)$$
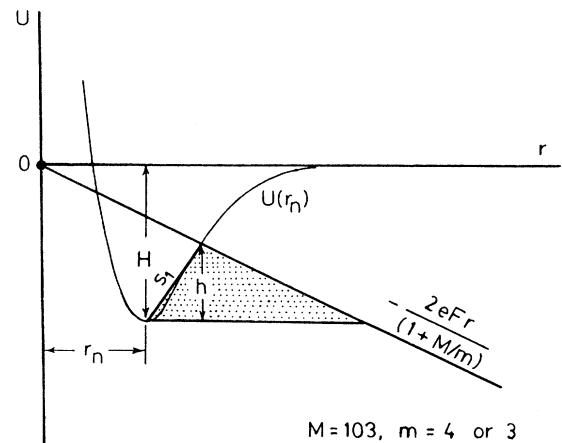
where h is the barrier height. The interaction between

FIG. 4. Schematic diagram showing the potential barrier in the field-dissociation process.

TABLE I. Values of $D(h,F)$.

F (V/Å)	$^4HeRh^{2+}$	$^3HeRh^{2+}$
4.8	1	2.4×10^{-9}
4.7	0.65	$< 10^{-10}$
4.6	0.28	$< 10^{-10}$
4.5	0.09	$< 10^{-10}$
4.4	0.02	$< 10^{-10}$
4.3	0.01	$< 10^{-10}$

He and Rh^{2+} should be very short ranged, and thus $1/s_1 \ll (1 + M/m)/neF$ and the $1/s_1$ term can be omitted. Figure 1(b) shows that at ~ 4.5 V/Å, $D(h,F)$ should be a few percent; we therefore assume that for $^4HeRh^{2+}$, $h = 0$ and $D(h,F) = 1$ at $F = 4.8$ V/Å. The binding energy H of $HeRh^{2+}$ should be the same for ^3He and ^4He. H and h are related to each other by

$$h \approx H - 2eFr_n/(1 + M/m). \tag{4}$$

Using Eqs. (3) and (4) gives the barrier-penetration probability per barrier encounter for $^4HeRh^{2+}$ and $^3HeRh^{2+}$ at different fields as listed in Table I. This WKB calculation gives a dissociation rate of $^3HeRh^{2+}$ smaller than that of $^4HeRh^{2+}$ by several orders of magnitude. The calculated values of $D(h,F)$ are consistent with the experimental results. The rotation

time of $^3HeRh^{2+}$ should be $\sim 30\%$ shorter than that of $^4HeRh^{2+}$, and thus the correct orientation for field dissociation can be reached in a shorter time. However, even at the highest field, i.e., the field at the surface of ~ 4.8 V/Å, the tunneling probability is still much too small for field dissociation to occur. The calculation also gives the binding energy of $HeRh^{2+}$ as $H \approx neFr_n/(1 + M/m) \approx 2 \times 4.8 \times 2.6/26.75$ eV$=0.93$ eV, consistent with a theoretical calculation.[6]

In summary, a dramatic isotope effect has been observed in the field dissociation of $HeRh^{2+}$ which can be well accounted for with a WKB calculation. An interesting theoretical question is how the rotational speed of a compound ion changes discretely as a result of the torque of an applied field.

[1]J. R. Hiskes, Phys. Rev. **122**, 1207 (1961).

[2]J. R. Oppenheimer, Phys. Rev. **31**, 67 (1928).

[3]A. C. Riviera and D. R. Sweetman, Phys. Rev. Lett. **5**, 560 (1960).

[4]T. T. Tsong and Y. Liou, Phys. Rev. B **32**, 4340 (1985).

[5]See, for example, E. W. Muller and T. T. Tsong, *Field Ion Microscopy, Principles and Applications* (Elsevier, New York, 1969).

[6]M. Hotokka, T. Kindsted, P. Pyykko, and B. O. Roos, Mol. Phys. **52**, 23 (1984).