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THE EFFECTS OF VIBRATIONAL AND ROTATIONAL MOTION ON THE FIELD DISSOCIATION BY ATOMIC TUNNELING OF HeRh2+ IONS

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Abstract: When a compound ion is placed in an intense electric field, the potential barrier may be lowered to the extent that dissociation can occur via quantum mechanical tunneling (1). We have made a numerical study of the detailed atomic process of dissociation. When the molecular ion, HeRh2+2, is field evaporated from the surface, it cannot dissociate since it is in the wrong orientation. As the molecular ion rotates and vibrates, the probability of dissociation becomes non-zero when the angle of rotation lies in the range 90° < θ < 270°. The model calculations predict the existence of a field dissociation zone of width 124 Å with the peak in the dissociation located at 197 Å above the surface. These results are in excellent agreement with the experimental data of Tsong and Liou (2,3). In addition, the model calculations predict four dissociation peaks within this zone due to the vibrational motion of the ion. These fine structure lines in the secondary Rh2+ peak are separated on the average by 0.86x10^-13 sec, implying an‘average vibrational frequency of 1.2x10^12 Hz. Their relative intensities are 0.356, 1.00, 0.784, and 0.235. These fine structure lines in the secondary Rh2+ peak should be experimentally observable provided the stability and the resolution of the atom-probe are further improved by a factor of about five. We are in the process of making an improvement so that the vibrational features in the field dissociation can be directly observed in the time-of-flight spectrum.

I. INTRODUCTION

If a compound ion or molecule is placed in a time independent electric field, an external force may act which tends to separate the charges and oppose the attractive Coulombic forces. This effect gives rise to a lowering of the potential barrier which allows for the dissociation of the compound ion or molecule via tunneling, a process similar to the field ionization of an atom in a high electric field which was investigated by Oppenheimer (1).

The particular compound ion HeRh2+ has proved to be useful for investigating this process of field dissociation for the following reasons:

1) The ions appear to form right at the surface. These ions can be produced by low temperature (<100 K) field evaporation of a Rh tip in He of 1x10^-8 Torr or higher, in a field between 4.5 and 5.0 V/A. Each surface Rh atom in the more protruding position undergoes field absorption with a He atom. Thus, there is no free-space field ionization of hopping molecules.

2) The reduced mass of the system is small enough so that tunneling effects are important.

3) The first ionization energy of He is 6.5 eV higher than the second ionization energy of Rh2+ and, hence, the He atom in the HeRh2+ remains neutral and bound to the Rh2+ by van der Waals forces.

4) There is an orientational effect associated with the HeRh2+ ions. Since the He atoms are field absorbed atop kink site Rh atoms, the HeRh2+ ions are thus expected to be desorbed from the surface in the same orientation. This result gives rise to a distinct orientational effect in the dissociation zone and is evident in the time of flight spectrum.

The experimental apparatus used to study this effect was a pulsed-laser time-of-flight atom probe field-ion-microscope (2,3). This system can achieve an accuracy and resolution of better than five parts in 10^6 or .3 to 1 eV out of 6 to 20 keV in ion energy measurements. This resolution was achieved by means of an ion reaction time amplification scheme by which the reaction time events which occur in a very short time have their detection stretched out over a longer period. The system is separated into three sections. In the first section the tip is placed with a grounded electrode 1.2 mm away. After passing through this section through an opening in the electrode, the ion travels through a field free region of length 4200 mm at a constant velocity. If two ions are created at slightly different times, and possess different kinetic energies when they pass through the electrode, they will have a large flight difference in the tube. With the arrangement used an amplification factor of about 4.8 x 10^3 is achieved.
The time-of-flight spectrum exhibits two well-resolved peaks for Rh$^{2+}$ with the higher energy peak more intense and separated from the low energy peak by 30 ns. Upon closer examination of the experimental features and theoretical analysis (3,4), one can conclude that the physical process is described schematically by:

$$\text{HeRh}^{2+} \rightarrow \text{He} + \text{Rh}^{2+}.$$  

From the time difference between the peaks, a kinetic energy difference of 51 eV was calculated by Tsong and Cole (4). Using a hyperboloidal approximation for the Rh tip, the field $F$ is given by

$$F(x) = \frac{V_0}{k_0 \left[ 1 + 2x/r_0 \right]}$$  

where $r_0$ is the tip radius taken to be 420 Å, $x$ is the distance from the tip, and $k$ is a geometrical factor taken to be 5. They concluded that the dissociation of HeRh$^{2+}$ occurs in zero of about 150 Å width centered at 220 Å from the tip surface.

The existence of a well-defined spatially localized zone for dissociation can be predicted from the following argument. The Schrödinger equation for the relative nuclear motion of He and Rh$^{2+}$ ion placed in an external electric field $F$ is:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(r_p) + \left[ U(r_p) - \frac{2eFz}{1+M} \right] \psi(r_p) = E \psi(r_p)$$

In this equation, $\mathbf{r}_p$ is a vector from He to Rh$^{2+}$, $\mu$ is the reduced mass, and $z_p$ is the component of $\mathbf{r}_p$ along $\mathbf{F}$, and $U(r_p)$ is the interparticle potential. Field dissociation can only occur if $z_p$ is positive; otherwise, the effect of the field is to decrease the internuclear equilibrium distance and increase the height of the tunneling barrier. As we have indicated earlier, however, the HeRh$^{2+}$ ion has the wrong orientation when it has just been desorbed from the surface. This is shown schematically in figure 1. The diatomic molecule is rotating and translating and when the angle reaches 90° and then increases to 180°, the probability of dissociation increases as well. As the angle increases from 180° to 270°, the probability of dissociation decreases to zero. If the ion does not dissociate during its first rotation, the ion must wait until its orientation is again between 90° and 270°. Calculations by Tsong and Cole (4) indicate that this requires a time of 2.370 ps, when the ion is 1350 Å away from the surface where the field has decreased to 0.65 V/Å (from the apex value of > 4.5 V/Å), a value much too low for field dissociation to occur.

In this paper, we discuss a numerical simulation of the process of dissociation. For these calculations, the interparticle potential given by Tsong and Cole (4) is used to evaluate the vibrational energy levels of the system. The tunneling is assumed to occur from the lowest vibrational state when the diatomic molecule has an orientation between 90° and 270° and the constituents are at the endpoints of their vibration. This semi-classical description of the process and model calculations predicts a spatially localized field dissociation zone which exhibits a fine structure that is the consequence of vibrational and rotational motion and the field distribution which gives rise to an ion orientation dependent tunneling probability.

II. NUMERICAL SIMULATION

In this analysis, the initial conditions are that the HeRh$^{2+}$ ion is evaporated from the surface in the wrong orientation for dissociation and the constituents are at the equilibrium distance from one another moving towards one another. Under the influence of the external electric field, the vibrational rate and amplitude vary as the molecular complex rotates and translates. The particle tunneling barrier varies with position (or time) and, hence, there is a position dependent transmission (dissociation) probability.

In order to evaluate the barrier as a function of time, the following set of equations must be numerically solved:

1) The equation of motion of the center of mass

$$\frac{dx}{dt} = \left( -\frac{eV_0}{k(m+M)} \right)^{1/2} \sqrt{\frac{1}{\ln \left( 1 + \frac{2z}{r_0} \right)}} \left( 1 + \frac{2z}{r_0} \right)$$

with $\frac{dx}{dt} = 0$ at $x = 0$. 

$$dx = \left[ \frac{eV_0}{k(m+M)} \right]^{1/2} \sqrt{\frac{1}{\ln \left( 1 + \frac{2z}{r_0} \right)}} dx \quad \text{with} \quad dx = 0 \text{ at } x = 0.$$

$$dx = \left[ \frac{eV_0}{k(m+M)} \right]^{1/2} \sqrt{\frac{1}{\ln \left( 1 + \frac{2z}{r_0} \right)}} dx \quad \text{with} \quad dx = 0 \text{ at } x = 0.$$
2) The equation of motion for rotation

\[ \frac{d^2 \theta}{dt^2} = \frac{2eF \sin \theta}{IM} \tag{4} \]

where \( \theta \) is the angle between \( r_n \) and the surface normal, and \( I \) is the moment of inertia.

The boundary condition is

\[ \frac{d\theta}{dt} = \omega_0 = \frac{2\sqrt{J(J+1)}}{I} \text{ at } t = 0. \]

3) The equation of motion for vibration

\[ \frac{d^2 r_n}{dt^2} = -\frac{1}{\mu} \frac{\partial U}{\partial r} \tag{5} \]

with \( r_n = r_{\text{equil}} \) at \( t = 0 \). The quantity \( U \) is the interaction potential between a He atom and Rh\(^{2+} \) ion which within the effective medium theory is given by (4):

\[
U(r_n) = \frac{8.395 \times 10^3}{r} e^{-(4.7732r)} - f_6 \left( 4.7732r \right) \frac{5.873 - f_6 \left( 4.7733r \right) 9.0946}{r^4} - f_6 \left( 4.7732r \right) \frac{25.52 - 2eF \vec{r} \cdot \vec{r}_n}{r^8} \frac{1}{(1+M/m)}
\]

where \( f_6(x) = 1 - e^{-x} \sum_{k=0}^{m} \frac{x^k}{k!} \)

The barrier penetration probability is calculated within the WKB approximation from:

\[ D(t) = \exp \left\{ - \frac{2m}{\hbar^2} \int_{s_1}^{s_2} \left[ U(r) - U(r_{\text{equil}}) - E_{\text{vib}} \right]^{1/2} dx \right\}. \tag{7} \]

The vibrational energy states from which tunneling can occur was calculated using a discretized-plane-wave method of solution of the Schrödinger equation (5) assuming that in zeroth order the vibrational energy levels are unaffected by the field. The results for the first four states are \( \epsilon_1 = 3.22 \times 10^{-3} \text{ eV} \), \( \epsilon_2 = 8.64 \times 10^{-4} \text{ eV} \), \( \epsilon_3 = 9.06 \times 10^{-5} \text{ eV} \), and \( \epsilon_4 = 1.92 \text{ eV} \), where the energies are relative to the bottom of the well. The two lowest vibrational states for an ideal harmonic oscillator would correspond to temperatures of 374 K and 1122 K, respectively. The rotational state of the molecular ion was assumed to be fixed at \( J=8 \), a value consistent with the most probable value of \( J \) assuming the laser irradiated surface temperature is 200 K.

III. RESULTS AND CONCLUSIONS

Equations (3), (4), (5) were integrated numerically using a fourth-order Runge-Kutta method to yield \( x(t) \), \( \theta(t) \), and \( r_n(t) \). The WKB penetration probability was then evaluated numerically as a function of time.

In figure 2, we display the results of our calculation of the argument of the transmission coefficient. Note that it is not symmetric about the peak due to the term \( -F \cdot r_n \) where \( F \) varies with distance from the apex (given by equation (11)). The barrier thickness is its smallest value at \( x = 211 \text{ Å} \). At values of \( x = 141 \text{ Å} \) and \( x = 301 \text{ Å} \), the thickness of the barrier increases by \( -0.65 \text{ Å} \) and the transmission coefficient is an order of magnitude smaller. Thus, the predicted zone of dissociation is about 160 Å wide and centered at about 208 Å above the tip.

In figure (3), we display the calculated vibrational displacement as a function of time. Within the region between \( 4.30 \times 10^{-13} \text{ sec} \) and \( 12.6 \times 10^{-13} \text{ sec} \), the average distance between the constituents is larger than the equilibrium distance in the absence of the external field. This produces a narrowing of the tunneling barrier and there is a marked increase in period of vibration. In this range, there are about 12 positions (and times) when the constituents are a maximum distance apart and there is the possibility for dissociation to occur.
In figure (4), we plot the results of relative probability as a function of time (position). The model predicts significant dissociation probability only at the following four times and positions:

- \( t_1 = 6.50 \times 10^{-13} \) sec, \( x_1 = 159 \) Å,
- \( t_2 = 7.43 \times 10^{-13} \) sec, \( x_2 = 197 \) Å,
- \( t_3 = 8.29 \times 10^{-13} \) sec, \( x_3 = 239 \) Å,
- and \( t_4 = 9.13 \times 10^{-13} \) sec, \( x_4 = 283 \) Å,

with relative intensities of 0.6, 0.784, and 0.335, respectively. These peaks are separated on the average by \( 8.86 \times 10^{-13} \) sec, implying an average vibrational frequency of \( 1.2 \times 10^{13} \) Hz. This data predicts that the dissociation zone is only about \( 124 \) Å and should consist of a fine structure of four lines.

From the computer simulation, in figure (5), we show schematically the orientation of the molecule at the four positions when dissociation may occur. Note that the orientation of the molecule for significant probability of dissociation is not symmetric about \( \theta = 180^\circ \) and calculations indicate that on the average out of 100 molecules that dissociate 90 will dissociate for \( 90^\circ < \theta < 180^\circ \). This effect is due to the combined effect of rotation and the field variation with position.

In summary, we have made a computer simulation of the detailed atomic process of dissociation. When the molecular ion, \( \text{HeRh}^{2+} \), is field evaporated from the surface, it cannot dissociate since it is in the wrong orientation. As the molecular ion rotates, translates, and vibrates, the probability of dissociation becomes non-zero in the range \( 90^\circ < \theta < 270^\circ \). The model calculations predict the existence of a field-dissociation zone of width \( 124 \) Å with the peak about \( 197 \) Å from the surface. This result is in excellent agreement with the results of Tsong and Liou (2). In addition, the calculations predict a fine structure in the zone consisting of four lines in the secondary Rh peak separated on the average by \( 8.86 \times 10^{-13} \) sec, due to the combined effects of the rotation, vibration and translation of the molecular ion. These fine structure lines should be observable in the time-of-flight spectrum if the stability and resolution of the atom-probe are further improved by a factor of five. Such modifications are now underway.

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Fig. 2. The argument of the transmission coefficient vs time. The left and right vertical lines define the limits $\theta = 90^\circ$ and $\theta = 270^\circ$, respectively.

Fig. 3. The displacement as a function of time for HeRh$^{2+}$ ions above a field ion emitter surface of 420 Å radius.
Fig. 4. The relative probability of dissociation (normalized to value at $t = 7.43 \times 10^{-13}$ sec) as a function of time.

Fig. 5. The orientation of the HeRh$^{2+}$ ion at the four most probable positions for field dissociation.

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