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Hyperthermal Surface Ionization of Mercury from Pt(111)

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The Pt(111)-surface ionization of hyperthermal mercury atoms (4–10 eV) was studied in helium- and hydrogen-seeded supersonic molecular beams. In spite of the large energy difference of 4.7 eV between the atomic ionization potential and the surface work function, an efficient ionization was observed. The ionization mechanism is discussed in terms of an extensive energy transfer to the surface and the creation of a transient local hot spot. Analytical applications are mentioned.

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Surface ionization (SI) is a well-known and established phenomenon.[1-6] However, its analytical applications are limited to the detection of a limited number of elements only[1-6] and some groups of organic molecules with a low ionization potential such as amines.[5,6] These limitations stem from the exponential reduction of the ionization yield with the difference between the atomic ionization potential and the surface work function ($I_p-\phi$). The effect of an atom's incident kinetic energy on its surface ionization was studied by Stein and Hurlbut[7] almost 30 years ago. Since then it was elaborated upon by many authors.[8-12] It was generally found that in the case of alkali metals such as sodium (Na) or potassium (K) and surfaces such as W(110) (Ref. 11) or Si(111) (Ref. 12) which were kept at relatively low temperatures, the ionization yield increased rapidly with the atomic kinetic energy above a certain threshold. These experiments were involved with atom-surface systems which could yield appreciable ionization under conventional thermal conditions due to their small or negative ($I_p-\phi$).

Danon and Amirav have found[13-20] that molecular kinetic energy can effectively bridge over the energetic requirements imposed by the Saha-Langmuir equations even for molecule-surface systems which are conventionally unamenable for surface ionization such as organic molecules.[16-18] The processes of hyperthermal surface ionization (HSI) were classified as follows: (a) molecule-surface electron transfer yielding molecular positive ions; (b) surface-molecule electron transfer to produce molecular negative ions; (c) hyperthermal surface-induced dissociative ionization to produce positive and negative fragment ions; (d) surface-molecule proton transfer to produce $(M+1)^+$ ions;[16,19] and (e) chemically induced HSI (CIHSI) where collision-induced dissociation produced new species with favorable ionization properties such as a low ionization potential or a high electron affinity.[20] A notable example is the CIHSI of cyclohexane (C_6H_{12}) which resulted in a high yield of $(M-1)^+$ species due to collision-induced hydrogen-atom transfer to the Pt(111) or Re-O surfaces, followed by radical-surface electron transfer. In this way efficient ionization is achieved even though the molecular I_p is 9.8 eV, since the ionization potential of the radical is below 7 eV.

In this Letter we address the question of HSI of an atom such as mercury which possesses the highest ionization potential among all the metal atoms, 10.44 eV.[21]

HSI of an atom such as Hg seems more difficult than that of organic molecules in view of the lack of possible CIHSI pathways, and the expected massive energy transfer to the surface.[22-24] Mercury can be easily included in a molecular beam since it is highly volatile. Because of its high atomic mass it can be aerodynamically accelerated to high kinetic energies.

Mercury was introduced as a liquid in a small mass-spectrometric tube. It was heated to ~140 °C behind a ceramic nozzle which was differentially heated to the range 150–750 °C. The nozzle was a 80-μm hole in a ruby watch jewel.[25] The mercury-helium- (or hydrogen-) seeded beam was skimmed, doubly differentially pumped, and collimated into an ultrahigh-vacuum chamber (base pressure 2×10^{-9} Torr). The supersonic beam was square-wave modulated or chopped for lock-in amplification or time-of-flight measurements of the Hg kinetic energy.[26] Two quadrupole mass analyzers (QMS) (UTI-100C) served as detectors. One head was aligned with the molecular beam for kinetic-energy measurements, while the second head was positioned 2.5 cm from the Pt(111) single crystal at 45° to the beam direction. It served for the detection of ions produced on the Pt(111) surface. The crystal was biased at about 4 V and a negatively biased plate with a 4-mm hole in front of the QMS served to attract and focus the positive ions which emerged from the surface. The Pt(111) surface was cleaned by 10-keV fast-argon-atom bombardment followed by surface-annealing (900 K) and oxygen-treatment cycles ($P=2\times10^{-6}$ Torr at 600 K). The surface cleanliness was checked by Auger spectra (VG CLAM-100) and helium scattering. The surface temperature was maintained at ~800–900 K during the ionization experiments to avoid mercury contamination. Oxygen was added to the UHV chamber at a pressure of $\sim1\times10^{-6}$ Torr to keep the surface clean from organic impurities and to suppress mercury-induced alkali-ion emission. Under these conditions the surface was slight-

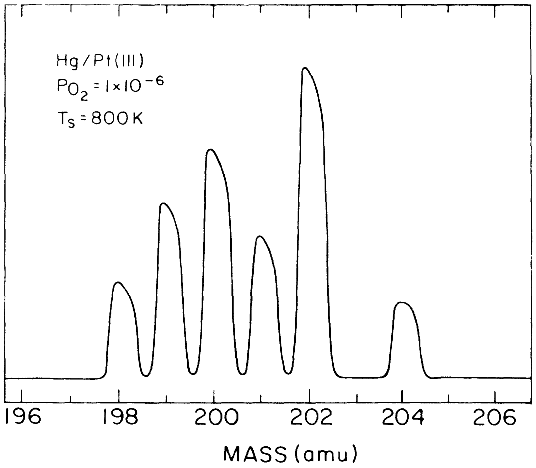

FIG. 1. Positive-ion hyperthermal-surface-ionization mass spectrum of mercury on Pt(111) single crystal. The mercury incident kinetic energy was ~7 eV and the beam was seeded with helium at ~800-K nozzle temperature. The surface temperature was also ~800 K and the background pressure of oxygen was 1×10^{-6} Torr.

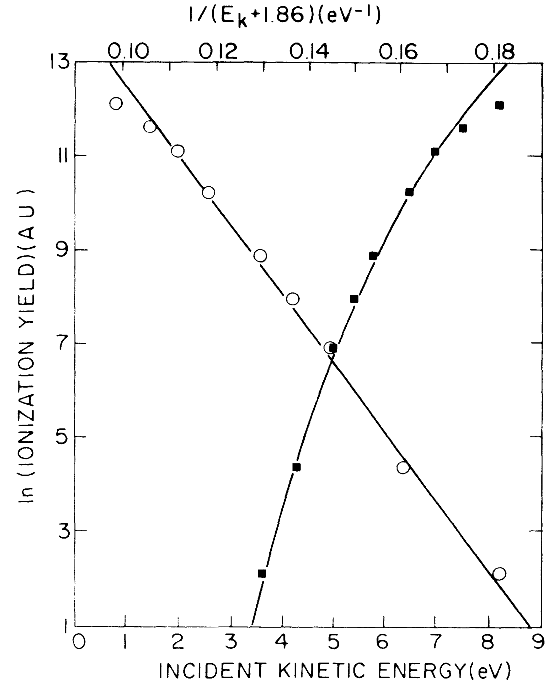

FIG. 2. The natural logarithm of the hyperthermal-surface-ionization yield of mercury on Pt(111) plotted against the mercury incident kinetic energy E_k (■) and vs $1/(E_k+1.86$ eV) (○).

ly covered with oxygen.[27,28] According to Derry and Ross[28] the surface coverage is below 5% of a monolayer at 800-K surface temperature.

Figure 1 shows the HSI mass spectrum of mercury in the range 196–206 amu. All the six prominent isotopes of mercury are observed with their exact natural abundance to within ±1.0% of the handbook values.[21] A closer inspection of the height ratio of an averaged mass spectrum (100 mass spectra on a Le-Croy 9400 signal averager) revealed a slight increase in the relative abundance of the heavier isotopes ($+\frac{1}{2}$%) and a similar slight decrease in the lighter isotopes. This is expected due to the linear increase in the atomic kinetic energy with the isotope mass. The minor (0.2%) 196-amu isotope was also observed. Figure 1 constitutes an unambiguous demonstration of hyperthermal surface ionization of an atom with an ionization potential of over 10 eV, such as mercury, at "moderate" incident kinetic energies of ~7 eV. Our estimated ionization yield using helium as a carrier gas at 8.2-eV incident kinetic energy was $\sim10^{-6}$–10^{-5} based on ion current, mercury consumption rate, and beam collimation values.

In order to obtain a better understanding of the ionization mechanism we have studied the HSI-yield dependence on the mercury-atom incident kinetic energy. Figure 2 is a plot of the ionization yield on a natural-logarithmic scale against both the Hg incident kinetic energy and $1/(1.86+E_k)$ (E_k in eV and the value 1.86 will be explained later on). A dramatic effect of E_k on the promotion of HSI is observed, and the ionization yield increases by almost 5 orders of magnitude in the kinetic-energy range 3.6–8.2 eV. A linear fit is observed in the logarithmic plot of $\ln Y$ vs $1/(1.86+E_k)$. On the other hand, we could not fit the yield by the form $y=k(E_k-4.74)^n$, where 4.74 eV is the expected threshold based on the energy requirement of $I_p-\phi=10.44-5.7=4.74$ eV. Even considering a possible oxygen coverage that increases ϕ by less than 0.3 eV,[28] the threshold behavior could not be accounted for. Thus according to Fig. 2, the direct atom-surface electron transfer mechanism seems to be unfavorable. Several possible artifacts can rationalize the signal from low-kinetic-energy atoms. (We note that even the 3.6-eV point is due to over 50 ions/sec without ion noise when the beam is turned off.) (a) Mercury dimers could produce the lower-kinetic-energy points since they might exist at the lower nozzle temperatures. (b) Intranozzle organic impurities can have a low threshold energy for their HSI. (c) The higher-energy tail of the seeded beam energy can prevail. However, we do not expect dimers at nozzle temperatures of above 500 °C in our simple nonconical nozzle and the exact isotope abundance exhibited precludes the involvement of organic impurities above E_k of 5 eV. In addition, the kinetic-energy distribution was narrower than our resolution (±8%). Thus, the good fit observed in Fig. 2 of $\ln Y$ vs $1/(1.86+E_k)$ over all the energy range (with the exception of the highest-energy point) suggests that the ionization proceeds via the "local hot spot" (LHS) mechanism. Accordingly the mercury atom scattered from a few platinum atoms and transferred most of its kinetic energy into local surface phonons. Extensive energy transfer to the surface by heavy atoms is well established.[22-24] The incident kinetic energy is transferred initially to the nuclear degrees of freedom of a few atoms n near the surface and increases their temperature by $\Delta E/3nk_B$ (k_B is the Boltzmann constant). If we assume total thermal equilibration between the mercury atom and the platinum atoms of the LHS, then the temperature rise is $E_k/3nk_B$ (n now includes the Hg atom) and the LHS temperature is $T_s+E_k/3nk_B$, where T_s is the surface temperature. We assume further that during the subpicosecond scattering period n is small and only after the scattering will the LHS grow and cool down. Implicit with the assumption of thermal equilibrium is the possible usage of the Saha-Langmuir (SL) equation to calculate the ionization yield. Ignoring entropy factors, we may approximate the HSI yield Y as

$$Y=\exp\left[-\frac{I_p-\phi}{k_BT+E_k/3n}\right]; \tag{1}$$

thus we obtain

$$\begin{aligned}\ln Y&=-3n\times 4.74/(3nk_BT+E_k)\\&=14.22n/(3nk_BT+E_k)\,,\end{aligned} \tag{2}$$

where 4.74 is the energetic requirement $I_p-\phi$ in eV. We have fitted $\ln Y$ vs $1/E_k$ and obtained n from the slope. Then in an iterative process n was introduced to the term $3nk_BT$ and finally the fit shown in Fig. 2 was obtained.

From this fit we have obtained $n\cong 9$ and a local hot spot temperature of 4200 K at 8.2-eV incident mercury kinetic energy. The extracted HSI yield at this energy is 2×10^{-6} which is in agreement with our estimated actual yield which is based on the mercury-ion current and its atomic beam flux. This agreement serves as an additional independent support to the validity of this mechanism. LHS is a well recognized mechanism in the quantitative description of the various ion yields in secondary-ion mass spectrometry[29] (SIMS). Amirav and Cardillo[30] have described electron-hole pair creation by hyperthermal xenon-atom scattering from InP(100) in terms of the LHS model. The main difference between the HSI of Hg and SIMS or the electron-hole pair-formation experiments is that in HSI the time duration of the LHS is well defined in terms of the scattering time scale. In addition, here we fit the HSI yield even below the $I_p-\phi$ energy which raises some difficult questions pertaining to the validity of this model in that particular form. (The incident kinetic energy has a narrow non-Boltzmann distribution.) These questions are beyond the scope of this Letter.

Hyperthermal surface ionization offers several important advantages over the conventional thermal surface ionization in its analytical applications.[17,31] (a) The ionization yield can be increased by many orders of magnitude. (b) The surface temperature can be much lower with a substantially reduced alkali and other background ion emission. (c) The variation in ionization efficiency among various elements or molecules can be much smaller and controlled. (d) Both negative and positive ions can be produced on the same surface. (e) There can be simpler and faster sample introduction at atmospheric pressure.

The observation of positive-ion HSI (PHSI) of mercury suggests that all the metal elements and many of the nonmetals are amenable to HSI as they possess lower ionization potentials than that of mercury. The combination of PHSI and negative-ion HSI (Ref. 17) seems to be possible for over 90% of the elements, practically all the organic molecules, and most of the inorganic molecules. Metal and alloy gasification can be aided by laser vaporization in supersonic jets.[32] The observed PHSI yield of mercury of $\sim 2\times 10^{-6}$ at 8.2 eV could be further increased up to 10^{-4} by the use of hydrogen carrier gas, but the yield was unstable due to oxygen removal from the platinum crystal by the hydrogen carrier gas which lowered the yield to 10^{-5}. A further PHSI yield increase is expected on a surface such as rhenium-oxide with a work function of 6.4 eV[4,6] and a higher tolerance to hydrogen gas at low temperatures. The nozzle can also be heated to well above 1000 K and E_k can be doubled in this way. Finally, we note that the PHSI of mercury was also involved with some alkali (Na, K) ion ejection.[33] When an atom with even higher ionization potential such as xenon ($I_p=12.13$ eV) was scattered from the Pt(111) surface, new species of NaXe^+ and KXe^+ were detected.[34] With mercury this alkali-impurity-ion abstraction was also observed but at a considerably lower yield as compared with bare mercury ions.

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