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*3 March 1982*

Dear Mr. Keith:

Enclosed is a copy of the final technical report for contract N00014-79-0855, concerning Photon Stimulated Ion Desorption, and supported from September 1979 to October 1981 by the Office of Naval Research. This project was a joint project by the University of California and the Naval Weapons Center.

Sincerely

*Christopher C. Parks*

Christopher C. Parks

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cc: P. Hannahs, Sponsored Projects Office  
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Technical Report on ONR Contract N00014-79-C-0855  
Concerning Photon Stimulated Ion Desorption

Christopher C. Parks  
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March 3, 1982

I. INTRODUCTION AND SUMMARY

This report summarizes a joint project by the University of California and the Naval Weapons Center, funded through Contract N00014-79-C-0855 from the Office of Naval Research (ONR). The project was supported from September 1979 to October 1981 by ONR, and concerned a newly discovered surface science technique, Photon Stimulated Ion Desorption (PSID). The goals in the project were of two types: (1) performance of experiments using existing and borrowed equipment and (2) development of a time-of-flight angle resolved PSID spectrometer.

The report will include a brief description of PSID, a description of experiments performed, and status of the apparatus under construction.

II. SCIENTIFIC BACKGROUND

When a surface is irradiated with photons in a certain energy range, ions are observed to desorb from the surface. This process is called Photon Stimulated Ion Desorption. Knotek, Jones, and Rehn<sup>1</sup> demonstrated direct PSID for the first time using synchrotron radiation. This discovery provided strong support for an Auger decay mechanism recently proposed by Knotek and Feibelman<sup>2</sup> to explain electron stimulated desorption (ESD), a related technique in which ions desorb from a surface upon excitation by electrons. Crucial to the discovery of PSID was the development of the time-of-flight technique, which allowed a high sensitivity and

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simultaneous data collection of all ions. Previous attempts to observe ions had not been successful.<sup>3</sup> It was anticipated, in analogy to ESD, that angular distributions of the ions leaving the surface would have a direct relationship to the bonding geometries on the surface.

The Auger decay model implies that the ion desorption yield should be proportional to the photon absorption cross section. This has the following two consequences: (1) It is possible to determine which substrate atom the desorbed ion came from. For instance, considering water adsorbed on  $TiO_2$ , a large increase in hydrogen yield from below to above the oxygen 1s absorption edge could be attributed to hydrogen bonded to oxygen. In the same way, desorption of some adsorbate on GaAs may be able to indicate whether the adsorbate was bonded to the Ga or the As. Answers to these questions are of fundamental interest to surface scientists and to industry.

(2) The ion desorption yield as a function of photon energy should display oscillations known as Extended X-ray Absorption Fine Structure (EXAFS). Analysis of these oscillations yields nearest neighbor bonding distances of surface atoms.

In particular EXAFS using PSID should give site selective bond distances--the nearest neighbor bond distances from the specific substrate atom which the ion had desorbed from.

Finally, PSID has great sensitivity to certain atoms. PSID is one of the few techniques for studying hydrogen on surfaces and also is very sensitive to fluorine; in one study<sup>4</sup> fluorine was detected using PSID which was unmeasurable using a conventional surface science technique, Auger spectroscopy.

In summary PSID is a new surface science technique having a number



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of attractive features. It is sensitive to hydrogen and other atoms adsorbed on surfaces which, while of great importance, are difficult to study using conventional techniques. Ion angular distributions show promise in determining bond geometries, and EXAFS using PSID can give site selective bond distances. Clearly research for the future should follow along two lines: 1) Apply the technique to study properties of surfaces and 2) to try to extend understanding of the mechanism of PSID.

The Auger decay model, formulated to understand desorption from ionically bonded systems, must be examined for the cases of covalent bonding and physisorption. For these systems other mechanisms may be in operation.

### III. EXPERIMENTAL RESULTS

This section lists the experimental papers already published, papers in press, and works in progress and result of the ONR contract. These papers resulted from experiments performed from existing and borrowed equipment. The papers already published are included in an appendix.

The Chemical make-up of Nb and Nb<sub>3</sub>Sn Films<sup>5</sup> concerns superconductor surfaces, and PSID is used to characterize the surfaces of these films. Quite a number of ions are observed using PSID which are below the detection limits of Auger spectroscopy, confirming the usefulness of PSID in such studies.

Desorption from GaAs(110)/H<sub>2</sub>O is studied;<sup>6</sup> only hydrogen ions are observed. Desorption of hydrogen ions from amorphous ice<sup>7</sup> is part of an ongoing study of condensed gases, and it is hoped that an understanding

of PSID from hydrogen bonded and van der Waals systems will ensue. Photon stimulated ion desorption<sup>8</sup> from oxidized cerium shows strong pre-edge atomic-like resonances, and conclusions have been formulated concerning the valency of the hydrogen bonded cerium. An oxidation study of titanium has been performed. A comparison of the near edge structure<sup>9</sup> to PSID yield is being completed for BeO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. A detailed study of the Auger decay mechanism is in progress in the NaF system. The mechanism of PSID is reanalyzed<sup>10</sup> in the case of hydrogen in Pd(100).

#### IV. STATUS OF THE TIME-OF-FLIGHT ANGLE RESOLVED PSID SPECTROMETER

To exploit the advantages of angular resolved PSID while retaining the advantages of the time-of-flight method, a unique data analysis system was proposed. A position encoder system used in electron spectroscopy<sup>11</sup> was to be used in conjunction with a time-of-flight (TOF) analyzer.<sup>12</sup> In this way one would be able to collect ions desorbing in all directions and also acquire and distinguish all of the masses simultaneously. In contrast, a conventional mass spectrometer would be able to collect only a small angular range and only one mass at a time. Clearly the position encoding TOF analyzer would be several orders of magnitude more sensitive than a conventional mass spectrometer, bringing many experiments to the realm of possibility.

In addition the spectrometer would be capable of state-of-the-art low energy electron diffraction spectroscopy. Using a pulsed electron gun, ion kinetic energy distributions and angular desorption patterns could be obtained using ESD.

After the ONR contract was awarded, work began on constructing an angle resolving time-of-flight analyzer system. Electrostatics calculations were performed to determine an optimal geometry. Surface science equipment was purchased. This equipment included an ion pump, a gate valve, a LEED system, an ion gun, a titanium sublimation pump, an ionization control unit, and a sample manipulator. Two 75 mm microchannel plates and a large resistive anode were purchased for the analyzer. Position encoder electronics were fabricated and plans for the micro-channel plate detector assembly were drafted. A chamber was purchased and a cart built to house the system.

The funds provided were insufficient to finish the project. In particular, a turntable system, built on separate funds, remained unfinished and the data routing system necessary to process the time and position data had not been built.

#### V. FUTURE OF THE PROJECT

There remain two possibilities for the continuation of the project: (1) A limited amount of funds has been authorized for the construction of an elliptical electron energy analyzer by the D.A. Shirley group at University of California at Berkeley. The elliptical analyzer should also be useful in the study of PSD. In addition to pooling funds, a joining of these two projects would involve a larger number of students working to finish the project. (2) Victor Rehn and Richard Rosenberg at the Naval Weapons Center plan to apply for further funds to complete the project.

The project described in this report concerns development of an

important new technique in surface science. PSID can be used to study adsorbates such as hydrogen that are of major interest yet difficult to study by any other method; in addition, PSID has a bright future in the determination of surface geometries of adsorbates. The proposed detector represents a significant advance over existing equipment in terms of its angle and mass resolving capabilities combined with its high collection efficiency. Development of this experimental apparatus would enable a whole new class of PSID experiments to be performed and lead to a better understanding of adsorbate bonding on surfaces. It is very unfortunate that funding was not continued so as to enable the time-of-flight angle resolved spectrometer to be completed.

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## APPENDIX I

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## THE CHEMICAL MAKEUP OF Nb AND Nb<sub>3</sub>Sn FILMS\*

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We report the identification and distribution of impurities found in films of Nb and Nb<sub>3</sub>Sn which were grown by multiple-source electron-beam coevaporation. Both Auger-electron spectroscopy (AES) and photon-stimulated ion desorption (PSID) were used. The PSID results show large desorption yields of hydrogen from surface carbon, oxygen, silicon, and aluminum impurity sites on the Nb films. From the Nb<sub>3</sub>Sn films, the dominant PSID yield was again hydrogen, which desorbed primarily from surface oxygen sites. Only after removal of 1-6 nm of material by Ar-ion sputtering was O<sup>+</sup> observed to be desorbed from Nb. O<sup>+</sup> desorption from Sn was never observed. The AES results showed only carbon, oxygen, and a trace of aluminum impurities in either material. Using Ar-ion sputter etching, the depth profiles of these impurities within the films were measured.

### 1. INTRODUCTION

We report the first application of photon-stimulated ion desorption (PSID)<sup>1-3</sup> to the study of superconductor surfaces. In this recently developed surface-analysis technique, desorbed ions are mass analyzed by the highly sensitive time-of-flight method, and their desorption sites are identified by excitation thresholds associated with core levels of surface bonding partners. Thus, by observing the ion desorption rates vs photon excitation energy, positive identification of the desorbed ion with its surface-bonding partner may be made. The photo-desorption mechanism active in this case involves a single quantum excitation which yields a low-energy desorbed ion from the outermost atomic layer only.<sup>1,4</sup> Thus, PSID offers a highly sensitive, site-selective, surface-layer chemical analysis which does not perturb the surface appreciably.

### 2. RESULTS

**2.1 PSID.** The results of our PSID analysis of Nb films in the nearly as-produced state showed the dominant positive-ion species<sup>5</sup> desorbed to be H<sup>+</sup> which had been bonded to surface carbon, oxygen, silicon, or aluminum impurity sites, but not to Nb. Other ions desorbed at much lower rates were (in order of decreasing yield) O<sup>+</sup>, F<sup>+</sup>, Na<sup>+</sup>, CH<sub>3</sub><sup>+</sup>, OH<sup>+</sup>, CH<sub>2</sub><sup>+</sup>, CO<sup>+</sup>, H<sub>2</sub><sup>+</sup>, Cl<sup>+</sup>, and K<sup>+</sup>.

After *in situ* Ar-ion sputtering to remove 1-5 nm from the surface, the desorbed-ion mass spectrum changed significantly. The yield rates increased for H<sup>+</sup>, O<sup>+</sup>, and F<sup>+</sup>, while all other desorbed species either vanished or diminished. The H<sup>+</sup> yield rate doubled, while

the O<sup>+</sup> and F<sup>+</sup> yields increased 20- and 30-fold, respectively. Excitation spectra showed less C-H and Si-H sites and no Al-H. More O-H, C-OH, C-O, and Si-OH sites were observed, and weak Nb-H and Nb-O thresholds were observed.

A similar analysis of Nb<sub>3</sub>Sn films showed them to be somewhat cleaner in the nearly as-produced state. The dominant positive-ion species desorbed was again H<sup>+</sup>, which came mainly from surface oxygen sites. No Nb-H or Sn-H thresholds were observed. At much lower desorption rates were O<sup>+</sup>, F<sup>+</sup>, H<sub>2</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, NO<sup>+</sup>, and CO<sup>+</sup>.

After Ar-ion sputtering to remove 2-6 nm from the surface, the desorption spectrum changed dramatically, as shown in Figure 1. Desorption rates for H<sup>+</sup>, O<sup>+</sup>, and F<sup>+</sup> increased by factors of 7, 300, and 240, respectively. The excitation spectra showed thresholds for Nb-O and Nb-H sites. A careful search failed to reveal any evidence of desorption from Sn sites, however.

**2.2 AES.** Auger spectra were obtained on each surface *in situ* before and after sputter etching or oxidation. With the gentle (2 kV) sputtering ion beam used, only 1-6 nm of material was removed. The AES spectra showed a gradual reduction of carbon and oxygen impurity peaks accompanied by a gradual growth and sharpening of the Nb and Sn peaks. Neither C nor O peaks were sputtered away completely in the *in situ* surface treatments. Subsequently, quantitative AES sputter-profiling measurements were performed at China Lake which showed the best of samples to have nearly 5% each of C and O within the surface layer sampled by AES. These concentrations diminished by half after removal of about 5 nm of material and were below 1% in the bulk of the films.

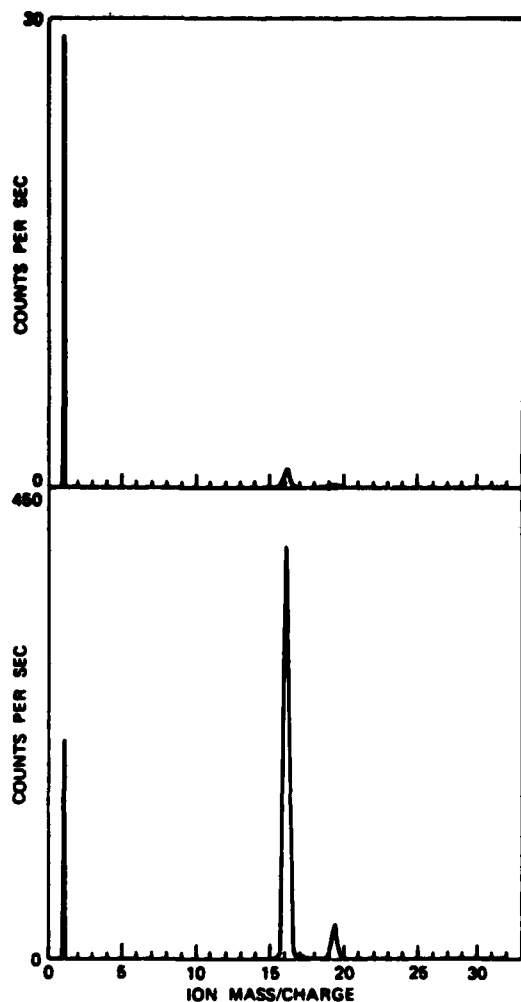


Figure 1 : Photon-stimulated ion desorption spectrum for  $Nb_3Sn$ . The upper spectrum is before sputtering, and the lower one is after sputtering. Several other mass peaks are too small to be seen on this scale (see text).

### 3. DISCUSSION

The samples studied were prepared for us at Stanford University<sup>5</sup> by multiple-source electron-beam coevaporation with feedback control.<sup>6</sup> The samples were packaged in  $N_2$ -filled plastic bags for transport and loaded within a few hours into the PSID chamber at the Stanford Synchrotron-Radiation Laboratory, where the PSID experiments were performed.<sup>7</sup> We baked the samples to  $500^\circ C$  during the chamber pumpdown: the lack of a nitrogen desorption pattern indicated that the effects of packing in nitrogen did not survive the bake.<sup>9</sup>

The huge increases in PSID yield rates after sputter etching must be attributed partly to the surface damage induced by the Ar-ion sputtering. For a single-quantum desorption mechanism, the probability of desorption is considerably greater at damage sites where the desorbed species is singly coordinated on the surface.<sup>2,3</sup> However, the greatly increased  $O^+/H^+$  yield ratio shown in Figure 1 cannot be accounted for on this basis alone, and we suggest that the sputtered surface has a much larger concentration of oxygen exposed in the outermost layer than the unsputtered surface. This effect was also observed on Nb films, but not so dramatically. Sputtering increased the yield rates of  $H^+$ ,  $O^+$ , and  $F^+$  ions from a Nb film by factors of 2, 20, and 30, respectively, and  $H^+$  remained the dominant species desorbed. These findings are in agreement with the conclusions of Miller *et al.*<sup>7</sup> who have proposed that the oxygen diffuses into Nb quite deeply, forming successive layers of  $NbO$ ,  $NbO_2$ , and  $Nb_2O_5$ , while in  $Nb_3Sn$  the oxidation process is self-limiting. Our inability to observe desorption from Sn-O sites could be evidence that these sites are not found on the surface or that desorption from them is unlikely for some other reason. Further work is required before the role of Sn-O sites in PSID can be determined.

\*We gratefully acknowledge the excellent collaboration of M. R. Beasley, R. Hammond, and T. H. Geballe who prepared films of Nb and  $Nb_3Sn$  for us. \*The Sandia National Laboratory is a Department of Energy facility. \*\*The Stanford Synchrotron-Radiation Laboratory is supported by the National Science Foundation in cooperation with the Department of Energy.

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PHOTON STIMULATED ION DESORPTION OF  $H^+$  IONS FROM GaAs(110)/H<sub>2</sub>O

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The photon stimulated ion desorption yield of  $H^+$  ions from a H<sub>2</sub>O dosed GaAs(110) surface has been measured in the range  $18\text{eV} \leq h\nu \leq 30\text{eV}$ . There is a direct correspondence between the PSID  $H^+$  yield, reflectance, and the secondary electron yield spectrum of GaAs(110). The data provides evidence that the initial stages of PSID involve core level (Ga(3d), O(2s))  $\rightarrow$  conduction band excitation followed by Auger decay.

Several studies of photon-stimulated ion desorption (PSID) from well characterised surfaces have now been carried out.<sup>1-5</sup> These followed from the first observation of PSID via  $H^+$  and  $OH^+$  PSID from a H<sub>2</sub>O dosed TiO<sub>2</sub> sample.<sup>6</sup> At the present early stage of development, the PSID technique holds promise for the site specific determination of adsorbate-substrate bond geometries and associated bond lengths.<sup>1-6</sup> To a large extent this is dependent on the applicability of the Knotek-Feibelman (KF) model of PSID (and ESD).<sup>7</sup> This supposes the initial step to be the creation of a core hole in a substrate or adsorbate atom, followed by inter- or intraatomic Auger decay from the adsorbate valence levels or adsorbate-substrate bond.

It has been argued<sup>7</sup> that the KF model will be most clearly observed in maximal valency ionic substrates, so that intraatomic Auger processes cannot occur on substrate atoms. Consequently, much of the previous effort has been concentrated in the study of ionic substrates or ionic adsorbate-substrate systems, e.g. oxygen on W(111).<sup>2</sup> If an ionic model is applicable, then after losing one or more electrons in the Auger process(es) the ionised adsorbate (anion) could be ejected into the vacuum by the Madelung site potential.<sup>7</sup>

The aim of the work described in the present communication was to investigate PSID from an adsorbate-substrate system where the bonding is likely to be relatively covalent, namely H<sub>2</sub>O dosed GaAs(110).

## Experimental

The experiments were performed on the 8<sup>o</sup> beam line ( $4\text{eV} \leq h\nu \leq 39\text{eV}$ ) at the Stanford Synchrotron Radiation Laboratory (SSRL). Under certain operating conditions, the pulsed nature of the source (0.4 ns width, 780 ns repetition period) allows the use of a time-of-flight (TOF) mass spectrometer in PSID studies. The TOF

apparatus employed is described elsewhere. A monochromator band-pass of  $2.5 \text{ \AA}$  was employed.

The Zn-doped ( $5 \times 10^{15} \text{ cm}^{-3}$ ) p-type GaAs sample was cleaved in a vacuum of ca.  $5 \times 10^{-10}$  Torr. A (110) surface of mirror-like quality was obtained. Following the cleave, a normal photoemission spectrum ( $h\nu = 25\text{eV}$ ) was recorded. The form of the spectrum is in accord with previous work.<sup>9</sup> PSID measurements were made after exposure of the surface (293K) to 4000 L of H<sub>2</sub>O ( $1\text{L} = 1 \times 10^{-6}$  Torr s). A grazing incidence geometry was employed, with the E vector at an angle of  $18^\circ$  to the surface normal. The front of the TOF drift tube was approximately parallel to the (110) surface. To avoid low level surface contamination, a LEED pattern was obtained following the PSID measurements. A well ordered surface was indicated by the (1x1) pattern observed.

## Results and Discussion

Little work has been carried out on the H<sub>2</sub>O dosed GaAs(110) system, although a recent UPES study tentatively concluded that H<sub>2</sub>O is molecularly adsorbed at 300K for exposures of  $< 10^4 \text{ L}$ .<sup>10</sup> At higher exposures physisorption is supposed to occur.<sup>10</sup> In this study, however, only  $H^+$  ions were detected in the PSID yield suggesting that at exposures of  $\leq 4 \times 10^3 \text{ L}$  H<sub>2</sub>O is dissociatively adsorbed on a GaAs(110) surface. However, it should be noted that only  $H^+$  ions are photodesorbed from amorphous ice. The variation in  $H^+$  PSID yield with photon energy is shown in Fig. 1. There is clearly a threshold for PSID at  $h\nu \approx 19\text{eV}$ , corresponding approximately to the threshold for Ga(3d)  $\rightarrow$  conduction-band excitation in bulk GaAs.<sup>11</sup> The structure in the  $H^+$  yield curve between  $21\text{eV} \leq h\nu \leq 24\text{eV}$  is similar to that observed in the secondary electron yield from GaAs(110)<sup>12,13</sup> and to the reflectance,<sup>14</sup> as shown in Fig. 1. These spectra mirror the density of bulk GaAs conduction band states<sup>12</sup> since the electrons

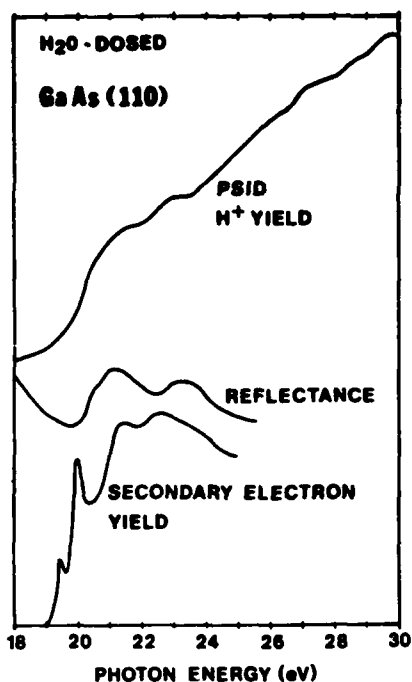


Figure 1

The  $H^+$  PSID excitation spectrum of  $H_2O$ -dosed GaAs(110) compared with the reflectance (after Ref. 14) and the secondary electron yield spectrum (after Ref. 15).

photoexcited into the conduction band,  $Ga3d_{3/2,5/2}$ , each have a band width of the order  $10^{-2}eV$ .<sup>15</sup> The two peaks at  $h\nu = 19.3, 19.8eV$  in the secondary electron yield spectrum arise from  $Ga3d_{3/2,3/2} \rightarrow$  surface exciton transitions.<sup>11,16</sup> The surface excitons are thought to decay by direct recombination,<sup>16</sup> a process which would not lead to desorption. However, it is possible

that an Auger decay channel is open, giving rise to  $H^+$ PSID at  $19eV \leq h\nu \leq 20eV$ , below the bulk threshold. Alternatively, it could arise from transitions from  $Ga(3d)$  into adsorbate induced states near the conduction band minimum. Structure in the  $H^+$  yield curve between  $24eV \leq h\nu \leq 31eV$  presumably arises from an initial optical excitation from  $O(2s)$  levels into conduction-band-like states. The difference in binding energy,  $BE_{O(2s)} - BE_{Ga(3d)}$ , for a GaAs(110)/-O surface at high coverage was found to be ca.  $4eV$ .<sup>17</sup> The doublet structure at  $25.8eV$  and  $27.3eV$  could arise from  $O(2s) \rightarrow$  conduction band excitation analogous to the  $Ga(3d) \rightarrow$  conduction band doublet at  $21eV$  and  $23eV$ , although the  $O(2s)$  levels are expected to be considerably broader than the  $Ga(3d)$  levels. The above interpretation of the  $H^+$  PSID yield curve suggests dissociative adsorption of  $H_2O$  on GaAs(110), forming Ga-H bonds. The -OH groups may be bonded to arsenic atoms. With the beam line used at S.S.R.L. desorption resulting from As(3d) excitation ( $h\nu > 43eV$ ) could not be probed, but  $OH^+$  desorption was not found in the Ga(3d) excitation region.

In so far as the KF model of PSID involves the creation of a core hole followed by Auger decay, it appears to be applicable to the  $H_2O$ -dosed GaAs(110) system. The mechanism for ion ejection from a covalent system presumably involves the creation, in the Auger process, of one or two holes in adsorbate-substrate bonding orbitals. These orbitals will have appreciable substrate atom character. Hence, PSID can still occur, even when the excited substrate atom is not in its highest formal valency state. PSID should therefore be a valuable technique in the elucidation of adsorbate-substrate covalent bond parameters.

Acknowledgment--This work was supported by the Science Research Council (U.K.), the U.S. Department of Energy under Contract No. AC (29-1)-767, the Naval Weapons Center Independent Research funds, and the U.S. Office of Naval Research. Experiments were conducted at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation in cooperation with the Stanford Linear Accelerator Center and the U.S. Department of Energy.

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## THE PHOTODISSOCIATIVE IONIZATION OF AMORPHOUS ICE

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Within the energy range  $17 < h\nu < 35$  eV, the ionic species desorbed and their excitation spectra are reported. The only positive ion desorbed is  $H^+$ . A model for the surface is suggested which explains the absence of  $OH^+$  desorption. The desorption mechanisms are discussed in terms of an energy analysis.

### 1. Introduction and summary

Recently Knotek et al. [1] demonstrated that photon-stimulated ion desorption (PSID) from fully valent ionic compounds proceeds primarily via a core-hole Auger-assisted mechanism. PSID has great potential as an extremely surface-sensitive technique, yielding information on the adsorbate bonding site and the local density of electronic states. Experiments to date have studied the interaction of various adsorbates with the surfaces of insulators [1,2], metals [3-6], and semiconductors [7]. However, no study has been reported of the photodissociative ionization of the pure, molecular solid. Such studies are a prerequisite for understanding the more complicated adsorbate systems.

As an initial experiment, we chose to study the photodissociative ionization of condensed  $H_2O$  (ice). Due to its abundance in the atmosphere,  $H_2O$  is

found on many surfaces in both dissociated and undissociated forms. Also, the large amount of hydrogen seen in ion desorption on nearly all surfaces could lead to  $H_2O$  or  $OH$  formation by reaction with residual atmospheric oxygen. In order to determine whether the ionic intensity distributions seen in past and future PSID experiments are due to molecular or dissociated  $H_2O$ , investigations in which the  $H_2O$  is known to be undissociated are imperative. The results presented here, together with recently initiated studies of  $H_2O$  isolated in inert-gas matrices, should greatly improve our understanding of these phenomena.

Ice is also known to be a major component of outer space. In fact, Saturn's rings are thought to be composed primarily of ice [8]. Ultraviolet "sputtering" is thought to be a primary process by which ice particles are evaporated [8]. The present study should be of great value as an aid to theoretical developments and interpreting experimental observations of outer-space and upper-atmosphere phenomena. Perhaps studies such as these may be used as a "fingerprint" for molecular  $H_2O$  and other species. We hope to

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extend these studies to higher energies and other molecular solids including those imbedded in inert-gas matrices.

The results of this work may be summarized as follows. The photodissociative ionization of amorphous ice was studied in the energy range  $17 < h\nu < 35$  eV. The only photodesorbed ion observed is  $H^+$ ; any  $O^+$  or  $OH^+$  desorption must be less than  $10^{-3}$  the  $H^+$  desorption yield. This observation supports a model of the ice surface that has hydrogen in the top layer. A model for the amorphous-ice surface is proposed which contains six types of sites, exclusive of defect sites. From three of these sites,  $H^+$  may be desorbed by a single-quantum process, but  $OH^+$  desorption is unlikely at all six sites. Examination of the yield spectrum reveals that desorption may proceed via the Knotek-Feibelman (KF) mechanism [9] or via a mechanism similar to that proposed by Menzel and Gomer [10] and by Redhead [11], the "MGR" mechanism.

## 2. Experimental

The basic experimental apparatus is shown in fig. 1. The variable-energy photon source was provided by the eight-degree line at the Stanford Synchrotron Radiation Laboratory (SSRL), which passed radiation in the range  $4 < h\nu < 35$  eV. A Seya-Namioka monochromator, operated with a 2.5 Å

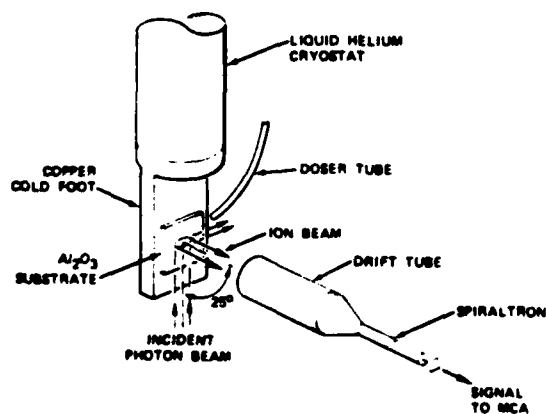


Fig. 1. Schematic of the apparatus used for PSID on cryogenic surfaces.

band pass, dispersed the incoming radiation. The ions were counted by a time-of-flight (TOF) detector similar to the one described earlier [1], which utilized the excellent timing properties of the synchrotron radiation at SSRL (pulse width  $\approx 0.3$  ns and interpulse period 780 ns). The detector described in ref. [1] was modified to improve field homogeneity and to allow the drift tube to be floated; thus, the drift-tube voltage ( $V_{dr}$ ) and therefore the ion energies and flight times could be varied independently of the voltage on the spiraltron ( $V_{sp}$ ). The results reported here were obtained at  $V_{dr} = 1650$  V and  $V_{sp} = 1800$  V, with a 3 cm drift tube situated 2 cm from the sample.

The ice films were grown by injecting degassed, triply distilled water vapor through a stainless steel doser tube onto an  $Al_2O_3$  substrate cooled to 6 K by liquid helium (fig. 1). These conditions are known to produce amorphous ice [12]. During the 10 min deposition period, the pressure in the UHV chamber rose from less than  $2 \times 10^{-10}$  Torr to  $5 \times 10^{-8}$  Torr. Within a few minutes of the cessation of film growth, the residual pressure was less than  $10^{-9}$  Torr. For some films, a continuous flow of  $H_2O$  producing a chamber pressure of  $\approx 1 \times 10^{-9}$  Torr ( $\pm 20\%$ ) was used to constantly refresh the surface. The TOF mass spectra of photodesorbed positive ions were taken at periodic intervals after growth of the films.

## 3. Results

In all spectra taken on a freshly prepared sample, the only detectable mass was  $H^+$ , in contrast to previously reported PSID results on  $H_2O$ -doped surfaces of insulators and semiconductors [1,2]. If the sample was allowed to age for several hours, higher-mass peaks (probably due to condensation of the ambient gas) could sometimes be detected; these peaks were always less than 1% of the  $H^+$  peak. In order to illustrate the difference in mass spectra between lightly  $H_2O$ -doped  $Al_2O_3$ , as studied in ref. [2], and an ice film grown on an  $Al_2O_3$  substrate, the following observation was made. The TOF mass spectrum was monitored continuously during the initial deposition of  $H_2O$  on the cold  $Al_2O_3$  ( $\approx 6$  K). Both  $H^+$  and  $OH^+$  ion peaks appeared immediately when  $H_2O$  deposition began. After  $\approx 100$  s (of the order of 1–10 L of exposure), the  $OH^+$  count rate dropped to zero

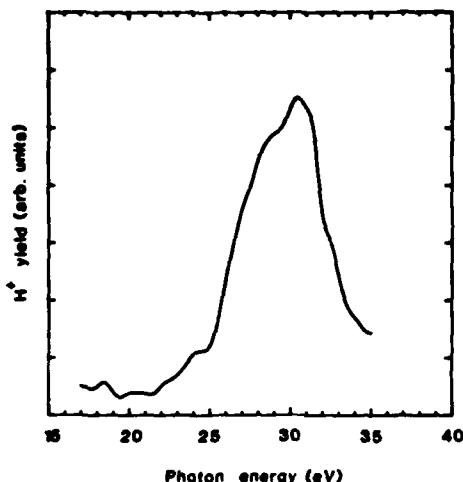


Fig. 2.  $H^+$  yield as a function of photon energy from ice at a temperature of 10 K. The data have been normalized to incident photon flux and smoothed.

and remained zero thereafter, while the  $H^+$  count rate remained strong.

In order to determine the excitation-energy dependence of the  $H^+$  yield, time-resolved excitation spectra were obtained [1]. A time window was set around the  $H^+$  peak, and the net area of the peak was plotted versus photon energy. The result, normalized to incident photon flux and smoothed, is shown in fig. 2. The  $H^+$  yield spectrum shows thresholds at 21.5 and 25 eV and a distinct shoulder at 33 eV. Structures seen near 29 eV varied from sample to sample, although some structure in the 27.5–30 eV was observed in every spectrum.

#### 4. Discussion

##### 4.1. Previous work

The only desorption studies previously reported on ice surfaces have used electrons as the excitation source. Madey and Yates [13] studied amorphous-ice films formed at 90 K on a Ru(001) surface using electrons in the range 100–200 eV. Their results show  $H^+$  to be the major desorption product, with higher masses being produced at a 1% level. They also reported the angular distribution of  $H^+$  desorp-

tion, which shows that the O–H bond is directed normally outward from the surface. Floyd and Prince [14] observed desorbing clusters of  $H^+(H_2O)_n$  ( $n = 3-9$ ) by bombarding ice condensed at 193 and 153 K with 80 eV electrons. They did not see cluster formation below 90 K, which is consistent with the findings of Madey and Yates and the present study. The photoabsorption spectrum of ice has been reported between 17 and 30 eV by Watanabe et al. [15]. Their results show a smooth, monotonic decrease in the absorption coefficient with energy except for a weak shoulder at 25 eV.

##### 4.2. Mechanisms

Currently there are two proposed mechanisms by which desorption from surfaces is thought to take place: the KF or Auger-assisted mechanism and the MGR or Franck–Condon gap excitation mechanism. From currently available theory, it is not possible for us to determine which mechanism is responsible for each structure observed in fig. 2. We will discuss possible contributions of KF and MGR mechanisms to the major features of fig. 2 based on energy considerations.

The relevant energy levels of bulk ice deduced from X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and ultraviolet absorption data [16–20]<sup>†</sup> are shown in fig. 3a, along with the molecular-orbital symmetry assignments. The band structure of cubic ice calculated by Paravicini and Resca [22] is shown in fig. 3b, along with the energy region in which Rydberg levels have been reported for free  $H_2O$  molecules by Goddard and Hunt [23] and others.

(i) The KF mechanism [9]. This desorption mechanism proceeds by a three-step process: (1) creation of a core hole (by photoabsorption in our case); (2) Auger decay of the core hole involving extraction of two or more electrons from the valence orbitals; and (3) coulombic repulsion of the ion from the surface due to its change of charge state. Both shallow [1] and deep [2,5] core holes have been shown to induce desorption via this mechanism.

<sup>†</sup> Note that the previously reported XPS results of Siegbahn et al. [21] have been reconciled by Baron and Williams [16] with corrections for surface charging to represent cubic ice.

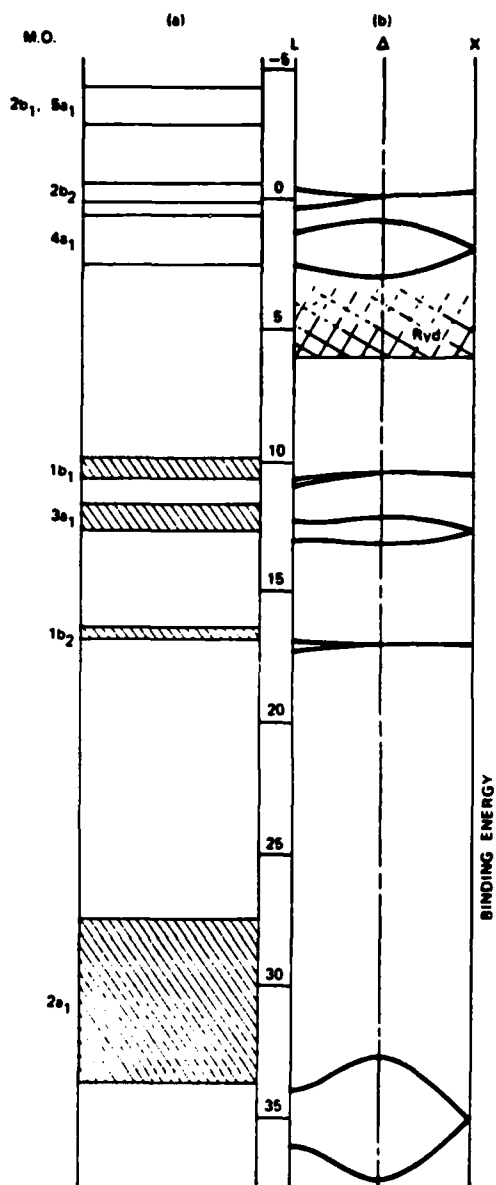


Fig. 3. (a) Electron-energy levels of bulk ice. (b) Electronic band structure calculated for cubic ice and the range of Rydberg levels in free  $\text{H}_2\text{O}$  molecules. Part (a) is deduced from the data of refs. [16–20]. The band-structure calculation is due to ref. [22], and the Rydberg states are reported in ref. [23].

In the case of ice, the shallowest core level ( $2a_1$ ) stems from the oxygen  $2s$  state, and appears to lie between 27 and 34 eV below the vacuum level (see fig. 3). Excitation of an electron from the top of the  $2a_1$  band to the lowest unoccupied state,  $4a_1$ , requires 25 eV excitation energy. Excitation to the hypothesized Rydberg levels would require at least 22 eV. Based on this energy analysis, it seems possible to explain the 25 eV threshold, the 33 eV shoulder, and possibly the 21.5 eV threshold shown in fig. 2.

However, this simple energy analysis neglects several important considerations. First, the bulk-ice energies shown in fig. 3 may not accurately represent the energies of states at desorption sites on the surface. Second, the Rydberg states of the free molecule may not survive condensation into an amorphous solid. Third, the Auger transition of the KF mechanism creates two or more valence holes at the desorption site, and an accounting must be made for the resulting energy of hole-hole repulsion, lattice polarization, and lattice relaxation. Finally, the altered-charge state of the desorbing ion must have a long enough lifetime for the desorption to take place, i.e.  $\tau \geq 10^{-12}$  s. None of these considerations have been adequately investigated, either theoretically or experimentally. Hence, it is not possible to evaluate their influence on KF-model desorption in amorphous ice.

(ii) The MGR mechanism [10,11]. This mechanism is the solid-state analog of free-molecule photodissociation, i.e. the excitation of the molecule to an unbound part of the ionic potential-energy surface. Photodissociative ionization of solids via the MGR mechanism has not been previously reported, although recent PSID experiments on  $\text{H}^+$  desorption from Pd in the range  $17 < h\nu < 34$  eV do indicate an MGR-like mechanism for that system [24].

Many experimental [25–30] and theoretical [31] studies of the photodissociative ionization of gaseous  $\text{H}_2\text{O}$  have been reported. The experimentally determined thresholds for production of  $\text{OH}^+$  and  $\text{H}^+$  are 18.1 and 18.7 eV, respectively. It is generally thought that “predissociation” of the  $\text{B}^2\text{B}_2$  level of  $\text{H}_2\text{O}^+$  is responsible for production of these ions [27–31].  $\text{OH}^+$  is created via the  $\text{X}^2\text{B}_1$  state and  $\text{H}^+$  via the  $\text{A}^2\text{A}_1$  state. The partial cross sections for production of both  $\text{OH}^+$  and  $\text{H}^+$  peak around 21 eV; at this ener-

gy, the  $\text{OH}^+$  yield is roughly five times the  $\text{H}^+$  yield [25].

The results on amorphous ice shown in fig. 2 are very different. The threshold energies and the shape of the  $\text{H}^+$  yield spectrum are *not* similar to the gas-phase results of ref. [25], and there is no  $\text{OH}^+$  produced. The lack of  $\text{OH}^+$  production can be understood by studying the desorption-site structure, as explained below. The 21.5 eV threshold shown in fig. 2 could be due to an MGR-type mechanism, possibly involving molecular predissociation as in the gas phase.

Apparently no theoretical or experimental work has been reported on predissociation in molecular solids. If this mechanism were to occur in ice, the predissociating level would be the  $\text{B}^2\text{B}_2$  level, as in the free molecule, which lies 16.5 eV below the vacuum level (see fig. 3). Shibaguchi et al. [19] claim that ice has a conduction band of high density of states lying 3.5 eV above the vacuum level. Although this claim is disputed by Abbati et al. [20], the energy difference between these two levels (20 eV) is close to the 21.5 eV threshold observed in fig. 2. However, even if this interpretation is essentially correct, it must be considered oversimplified, since there remain several small effects which cannot now be adequately evaluated.

For the major threshold at 25 eV, we find no energy levels by which an MGR-type photodesorption of  $\text{H}^+$  could occur.

#### 4.3. Surface structure

The surface structure of amorphous ice may be guessed from crystallographic data on ice. Although ice can crystallize in many forms, all are based on the tetrahedral coordination of the oxygen sublattice and a single hydrogen located along each O-O axis [32]. Thus, in the two common forms of ice, the oxygen sublattice is a diamond structure (cubic ice which forms between 135 and 160 K) or a wurtzite structure (hexagonal ice which forms above 160 K). Pauling [33] has shown that the low-temperature behavior of the entropy can be explained if three rules are followed: (1) The hydrogens are not centered in the O-O axis but are covalently bonded to one oxygen (bond length 1.01 Å) and hydrogen bonded to the other oxygen (bond length 1.75 Å). (2) There

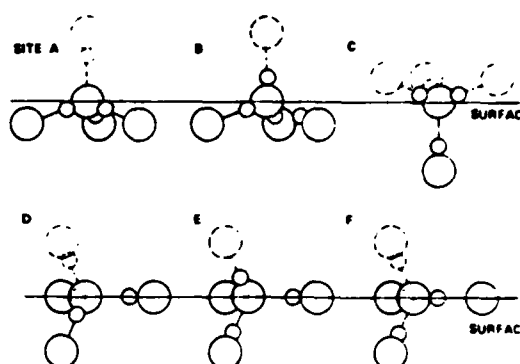


Fig. 4. Types of surface sites on amorphous ice. Although tilted randomly in the amorphous surface, the surface sites may be categorized as shown in terms of hydrogen placement relative to the surface plane. The large circles represent oxygen atoms, and the small circles represent hydrogens. Both atoms are scaled according to their covalent radii. The dashed circles above the surface show the locations of atoms needed to complete the tetrahedral coordination of the bulk solid.

are only two hydrogens covalently bonded to each oxygen. (3) The hydrogens are statistically distributed among the configurations allowed by rules (1) and (2). (The latter requirement also is necessary in order that the ice crystal not be ferroelectrically polarized.) From this picture of crystalline ice, one may guess that amorphous ice will be locally similar but with the long-range order broken as in amorphous Si or  $\text{SiO}_2$ .

Ignoring defect sites<sup>‡</sup>, the amorphous-ice surface should then have six types of sites distributed over the surface. These are shown schematically in fig. 4. Sites B, C, and E have hydrogen atoms "up" where they are accessible for desorption via single-quantum excitation, while sites A, D, and F do not. By contrast, the desorption of  $\text{OH}^+$  is unlikely at all sites due to the need to break two or three bonds.

It seems likely that both "H up" sites (B, C, and E) and "H down" sites (A, D, and F) occur on the amorphous ice surface, but not necessarily with equal frequency. Fletcher [34-36] contends that thermo-

<sup>‡</sup> Desorption at defect sites would be expected to yield a complex ion spectrum including  $\text{H}_2\text{O}^+$ ,  $\text{OH}^+$ , and  $\text{O}^+$ . The absence of these heavier ions is evidence for a low density of defect sites on the surface.

dynamical considerations favor the "H up" surface<sup>#</sup>. The amorphous ice surfaces formed at very low temperatures may not show the thermodynamically preferred distribution, but may be governed more strongly by non-equilibrium growth considerations. Our results confirm those of Madey and Yates [13] that there are outward-pointing O-H bonds on the surface, but do not rule out the existence of "H down" sites (A, D, and F) or sites with non-normal O-H bonds (sites C and E). The latter sites may be difficult to observe in the angular-distribution experiments due to the much larger solid angle into which these ions may be desorbed.

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<sup>#</sup> Fletcher's more recent model for the surface of high-temperature ice (263–273 K) has "H up" sites [34–36], in contrast to an earlier model [37] in which this surface was composed of "H down" sites. In the case of liquid H<sub>2</sub>O surfaces, Fletcher [35, p. 133] has discussed experimental evidence for "H down" sites.

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