OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0280

Task No. NR413E001

TECHNICAL REPORT NO. 34

Dissociative Adsorption of Ph₃ on Si(111)-(7x7) -

A High Resolution Electron Energy Loss Spectroscopy Study

by

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Submitted to

Surface Science

Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

August 7, 1990

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
34		

4. TITLE *(and Subtitle)*	5. TYPE OF REPORT & PERIOD COVERED
Dissociative Adsorption of PH_3 on Si(111)-(7x7) - A High Resolution Electron Energy Loss Spectroscopy Study	
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
P.J.Chen, M.L. Colaianni, R.M. Wallace and J.T. Yates, Jr.	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Surface Science Center Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
	August 7, 1990
	13. NUMBER OF PAGES
	21

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)*
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Phosphine, Silicon(111), Doping, Phosphorus, Dissociative

20. ABSTRACT

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Abstract

Dissociative adsorption of PH_3 on Si(111)-(7x7) has been observed at 80 K. The Si-H species is observed to be produced upon PH_3 adsorption. Depending upon the PH_3 surface coverage, $PH_3(a)$ (minority species) and $PH_2(a)$ species are found on the surface. The thermal dissociation of the surface PH_2 species occurs between 450 and 500 K, resulting in the capture of hydrogen and phosphorus on the surface.

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I. Introduction

Studies of simple hydride molecules (NH_3, PH_3, C_2H_2, C_2H_4, C_3H_6, B_2H_6, etc.) on silicon surfaces have received increasing attention in recent years [1-17] due to the involvement of molecules of this type in chemical vapor deposition (CVD) and doping of silicon. Vibrational spectroscopy is among the variety of surface analytical methods being applied to selected molecule/Si surface systems to monitor the adsorption and dissociation processes [6,7,11-13]. In the relatively well-studied system of NH_3 on Si surfaces, high resolution electron energy loss spectroscopy (HREELS) studies [11-13] have provided direct evidence for the dissociative adsorption of NH_3 on both Si(111) and Si(100). For the analogous molecule PH_3, however, such important information is not available, although rather detailed studies have been carried out using LEED, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) [1-5], and recently, temperature programmed desorption (TPD), kinetic uptake measurements and electron stimulated desorption (ESD) [16,17]. We present here a HREELS study of PH_3 adsorption and its thermal behavior on the Si(111)-(7x7) surface. Vibrational evidence for dissociative adsorption of adsorbed PH_3 species has been obtained at 80 K, confirming the results of other studies using other experimental methods at this temperature [16,17]. Additional P-H bond scission occurs at ~450 K; this is followed by H_2 desorption (~740 K) and P_2 desorption (~1000 K).

II. Experimental

The experiments were performed in a stainless steel UHV system described previously [18]. The typical system base pressure was $\sim 1 \times 10^{-10}$ mbar as measured with a Bayard-Albert ionization gauge. The UHV system is equipped with a single

pass CMA Auger electron spectrometer (AES) (Perkin-Elmer), a shielded quadrupole mass spectrometer (QMS) and a home built LEED apparatus. High resolution electron energy loss spectroscopy (HREELS) studies were conducted with a Leybold-Heraeus ELS-22 spectrometer interfaced to a digital data acquisition system [19]. The incident electron energy was ~6.5 eV and the total scattering angle was about 120°.

The Si(111) used in this study was a 13mm x 13mm x1.5mm, p-type, B-doped (10 ohm-cm nominal resistivity) single crystal oriented to within 1°. The crystal was cooled by liquid-N_2 to 80 K and could be resistively heated up to 1300 K as measured by a W/Re(5%)-W/Re(26%) thermocouple. The mounting and initial cleaning of the crystal using a standard chemical cleaning procedure is described elsewhere [16,20]. The final cleaning and preparation of the surface was achieved by Ar^+ sputtering at an energy of 1 keV and a current of 3 μA, followed by subsequent annealing at 1200 K and then, slow cooling back to 80 K. This procedure produces a well-ordered Si(111)-(7x7) surface with no impurities within the detection limit of AES.

The adsorption of phosphine gas was accomplished by using a translatable microcapillary array doser [20] contained in the UHV system. The PH_3 flux at the crystal was calibrated in the same fashion as described in a recent paper [17] by using the doser-crystal geometry and the PH_3 effusion rate into the doser. Correlation of the absolute full coverage for PH_3 adsorption in this apparatus with that measured elsewhere [17] was made to within 8% accuracy. It is determined that this full coverage corresponds to 1.9×10^{14} PH_3 cm^{-2}. This full (saturation) coverage may be achieved after an exposure of 2×10^{15} PH_3 cm^{-2} at 80 K [17]. To avoid any possible electron beam induced decomposition and electron stimulated desorption (ESD) effects during PH_3 adsorption, the ionization sources (ionization gauge, QMS) were turned off.

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III. Results and discussion

1. Phosphine adsorption on Si(111)-(7x7) at 80 K

Detailed kinetic studies of phosphine adsorption on Si(111)-(7x7) at 120 K have been reported in separate papers [16,17]. Uptake measurements show that phosphine adsorption proceeds with a constant sticking probability (S=1) up to 1.5×10^{14} PH_3 molecules cm^{-2} (i.e. ~75% of the saturation coverage), indicating an extrinsic mobile precursor adsorption mechanism. Additional PH_3 adsorbs with reduced sticking probability until saturation is reached at 1.9×10^{14} PH_3 molecules cm^{-2}. Similar PH_3 uptake experiments conducted in this work at 80 K agree well with the above results, where an independent absolute calibration of the doser in this apparatus has been made.

Figure 1 shows the HREEL spectra from the clean and PH_3-exposed Si(111)-(7x7) surface under specular electron scattering conditions. It is well knowr that the clean Si(111)-(7x7) surface exhibits a broad, temperature depenaent, energy loss tail which is associated with the Si(111)-(7x7) surface electronic structure (see Fig. 1(a)) [21]. Upon PH_3 adsorption, this broad energy loss tail is removed (Fig. 1(b)-(e)). For the PH_3-covered surface, energy losses are observed at 495, 600, 1050, 2060 and 2260 cm^{-1}. The 2060 cm^{-1} mode is readily identified as the Si-H stretching mode, $v(SiH)$, by comparison with the now well-known H/Si(111) system [22], and its presence is thus indicative of PH_3 dissociation upon adsorption at 80 K. The shoulder at ~600 cm^{-1} is the corresponding Si-H bending mode, $\delta(SiH)$, in the monohydride phase. Detailed assignments will be given to all the modes in the following paragraphs.

There is other experimental evidence indicating some dissociation of PH_3 into PH_x ($2 \geq x \geq 1$) species on Si(111)-(7x7) at low temperatures based on recent Auger electron spectroscopy studies [16]. In this work, the silicon bulk

plasmon loss feature accompanying the 92 eV Si(LVV) Auger transition exhibits changes characteristic of the presence of chemisorbed H after PH_3 adsorption at 120 K. This change in the plasmon loss intensity is enhanced upon warming of the surface to ~500 K as further P-H bond scission occurs [16]. The HREELS observation of the presence of the Si-H stretching mode upon PH_3 adsorption provides conclusive evidence for dissociative adsorption. However, in order to further identify the surface $PH_x(a)$ species, it is informative to compare our measurements with some infrared (IR) and HREELS data for certain systems containing PH_3, PH_2 and PH moieties. A selective list of results is shown in Table I.

HREELS studies of PH_3 chemisorbed on Pt(111) by Mitchell et al [23] show the PH_3 stretching frequency at 2325 cm^{-1} and the two PH_3 deformation modes (symmetric and asymmetric) at δ_s = 985 cm^{-1} and δ_d = 1080 cm^{-1} (non-dipole active) respectively. On the other hand, IR studies of PH_2-containing compounds (silyl and methyl phosphine, SiH_3PH_2, CH_3PH_2, diphosphine, P_2H_4 [25], and silanyl phosphine, $Si_2H_5PH_2$ [26]) report a PH_2 deformation (scissors) mode $\delta(PH_2)$ in the range 1069 - 1093 cm^{-1}, a PH_2 stretching mode, $\nu_s(PH_2)$, in the range 2300 - 2310 cm^{-1}, and a Si-P stretching mode, $\nu(SiP)$, in the range 454 - 515 cm^{-1}. Based upon these known frequencies, we assign the 495 cm^{-1} mode in our HREEL spectra as the Si-P streching mode, $\nu(SiP)$. The vibrational modes at 1050 and 2260 cm^{-1} are assigned to surface $PH_2(a)$ species, with some possible contribution by $PH_3(a)$. In particular, the 1050 cm^{-1} mode can belong to the scissors deformation mode of the $PH_2(a)$, $\delta(PH_2)$, with a possible contribution from the (positively-shifted) symmetric deformation mode of the $PH_3(a)$, $\delta_s(PH_3)$, since off-specular measurements (not shown) indicate that it is due to dipole scattering and its frequency is not a decisive indicator of its origin.

The following experimental facts are important in clarifying the identities

of the surface PH_x(a) species: (1) the presence of the Si-H mode strongly

suggests, even at 80 K, the dissociation of PH_3, i.e. the presence of PH_2(a)

and/or PH(a) on the surface; (2) temperature programmed desorption (TPD)

measurements from intermediate to saturation initial coverages of PH_3 on

Si(111)-(7x7) [17] also reveal the desorption of small quantities of

(non-recombinative) molecular PH_3(g), indicating the presence of molecular

PH_3(a) on the surface. The surface concentration of the PH_3(a) species,

however, is believed to be rather low [17]. Therefore, for PH_3 coverages above

1.5×10^{14} cm^{-2} where molecular PH_3 desorption can be detected by TPD, the

coexistence of PH_3(a) and PH_2(a) species on Si(111) surface yields the observed

energy loss features at 1050 and 2260 cm^{-1}. For PH_3 coverages below 1.5×10^{14}

cm^{-2}, the predominant surface species is PH_2(a) with very little or no PH_3(a),

although the spectroscopic evidence for this is not totally conclusive.

Another surface species candidate, PH(a), is not preferred in our

interpretation of the HREEL spectra. A survey of infrared studies of

PH-containing compounds shows that, unlike the PH_2-containing compounds, there

is quite a variation in the observed P-H deformation frequency δ(PH). Some

simple compounds such as $(CH_3)_2PH$ and F_2PH exhibit P-H deformation frequencies

at 998 cm^{-1} and 1016 cm^{-1} respectively [27,28]. Other PH ligands as in $(CF_3)_2PH$

and $(CF_3S)_2PH$ exhibit a much lower P-H deformation frequency at 850 cm^{-1} and 894

cm^{-1} [29] respectively. A variety of secondary phosphines containing

substituted aryl (R_1) and phenyl (R_2) groups of the general formula R_1R_2PH also

exhibit P-H deformation modes in the range 886-897 cm^{-1} [30]. Assuming that

δ(PH) modes in the 850-897 cm^{-1} range are analogous to that of a PH species

adsorbed on Si(111), we can eliminate PH(a) as a candidate species responsible

for the 1050 cm^{-1} mode in our HREEL spectra. Such an argument is further

supported by the experimental observation that, upon total thermal decomposition

of the $PH_x(a)$ species, the intensity of the silicon-hydrogen stretching mode $\nu(SiH)$, undergoes more than a 3-fold increase compared to its initial intensity at 80 K (detail in next section). Considering the rather low initial concentration of surface hydrogen species H(a) at 80 K, such a large increase in H(a) can only be accounted for by the decomposition of $PH_2(a)$ species rather than PH(a). Of course, this does not exclude PH(a) from being a minority species on the surface at 80 K. Based upon the above discussions, we assign the 1050 cm^{-1} mode as $\delta(PH_2)$.

HREELS studies of an analogous molecule, NH_3, on the Si(111)-(7x7) surface [11] have reached a similar conclusion that NH_3 dissociates into $NH_2(a)$ and H(a) at 300 K. Additionally, electron stimulated desorption ion angular distribution (ESDIAD) and TPD studies of NH_3 chemisorbed on Si(100) have shown that NH_2 is the dominant surface species produced [14,15]. Therefore, the bonding of the $PH_3(NH_3)$ molecules to the Si(111) surface occurs through the scission of one of the P-H(N-H) bonds instead of surface bonding through the phosphorus(nitrogen) lone pair electrons. This is in contrast to the case of $PH_3(NH_3)$ bonding to metal surfaces [23,24] where undissociated bonding involving the lone pair electrons is found. Dangling bond site capping experiments involving atomic deuterium have demonstrated that the active sites for both PH_3 [17] and NH_3 [15] adsorption are the Si dangling bonds.

2. Thermal behavior of the phosphine-derived overlayer

As previously mentioned, thermal desorption studies of adsorbed phosphine on Si(111)-(7x7) reveal two reaction pathways (Figure 2). In the first pathway, molecularly adsorbed PH_3 desorbs as $PH_3(g)$, forming a broad desorption feature extending to 550 K. The quantity of PH_3 desorbing is a small fraction of a monolayer [16,17]. In the second pathway, surface $PH_2(a)$ species thermally

decompose ultimately into P(a) and H(a), which subsequently desorb as $P_2(g)$ and $H_2(g)$. H_2 desorption is observed from 650 to 850 K with the peak temperature at ~740 K. P_2 desorbs from 900 - 1100 K. In the current work, HREELS has also been used to monitor the thermal behavior of the surface $PH_2(a)$ species. Figure 3 shows the HREEL spectra taken at 80 K after sequentially heating the PH_3-exposed Si(111) surface to specified temperatures. By heating in the temperature range of 80 - 450 K, an intensity decrease in the $\nu(PH_2)$ stretching mode at 2260 cm^{-1} signifies the breaking of additional P-H bonds. In the temperature range 450 - 500 K, by contrast, a major increase in the intensities of the Si-H stretching mode at 2070 cm^{-1} and Si-H deformation mode at 630 cm^{-1} is observed. Because of the large increase in the intensity of the Si-H stretching vibration after total thermal dissociation, it is likely that the majority species on the surface are H(a) + $PH_2(a)$ in the temperature range 80 - 450 K rather than 2H(a) + PH(a). We do not understand why the $\nu(PH_2)$ mode seems to decrease in intensity mostly in the low temperature range; this may be due to a structural rearrangement on the surface. The decrease of intensity in the 1050 cm^{-1} $\delta(PH_2)$ mode, mainly in the temperature range 450 - 500 K, is also indicative of PH_2 dissociation, possibly into PH(a) and H(a). However, based upon our HREELS data, we are unable to make a clear identification of the PH(a) species due to the likely overlap of its spectral features with those of $PH_2(a)$ and our limited instrumental resolution.

For a saturation PH_3 exposure ($2x10^{15}$ molecules/cm^2), it can be seen from comparison of Figure 2 and Figure 3 that the desorption of a small amount of molecular $PH_3(g)$ in the temperature range 80 - 550 K during heating does not seem to have a noticeable influence on the observed frequencies of the main spectral features, except for the background intensity increase observed between 80 and 200 K. The nature of this broad background increase in the HREEL spectra

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after heating the PH$_3$-covered surface to 200 K is not currently understood. It has been consistently observed in all of our heating experiments with low and high initial PH$_3$ coverages. A similar background is also observed in our PH$_3$ adsorption studies at 300 K (discussed below). The possibility of surface contamination during the course of HREELS analysis can be ruled out by the fact that leaving an unheated overlayer in the UHV system for an extended length of time does not cause such a background increase. Therefore, we tentatively attribute this broad background to some unknown electronic transition processes associated with the PH$_2$(a) + H(a)/Si(111) layer.

Significant changes in HREEL spectra occur between 450 and 500 K where the two Si-H vibrational modes at 630 and 2070 cm^{-1} dominate the spectrum after heating to 500 K. Complete dissociation of the PH$_2$(a) species into P(a) and H(a) occurs in the above temperature range. This behavior, in which additional Si-H species are produced, corresponds closely to the results of AES lineshape studies of the Si(LVV) transition from this laboratory [16], where the maximum surface hydrogen coverage derived from PH$_x$ adsorbed species has been observed to occur at ~500 K. It also correlates very well the observed drop in the H$^+$ ESD yield from PH$_x$(a) above ~400 K in the same work [16], as PH$_2$(a) species dissociate.

Further heating of the Si(111) surface results in the desorption of H$_2$(g) between 650 - 850 K, leaving only P(a) on the surface as determined by Auger measurements. The quality of the HREEL spectra in the temperature regime (900 - 1000 K) is rather poor, suggesting disorder on the surface. The spectral feature at ~450 cm^{-1} agrees with the literature value for an Si-P stretching vibration [31] while the origin of the weak feature at ~900 cm^{-1} is less clear. It may belong to some subsurface Si-P vibrational mode(s), since both features at ~450 and ~900 cm^{-1} are enhanced after several heating-PH$_3$ readsorption cycles

between 80 and 900 K (not shown), where an increasing phosphorus concentration is seen with AES measurements. These AES studies have shown that there is evidence for substantial P penetration into the near surface region under these heating-readsorption conditions [17].

3. Adsorption of phosphine on Si(111)-(7x7) at 300 K

Yu and Meyerson [4] have reported PH_3 adsorption studies on the Si(100) surface at room temperature with an initial sticking coefficient S_0 of the order of unity. Based on further XPS and thermal desorption studies, Yu et al [5] have suggested that PH_3 adsorbs mostly undissociatively on Si(100) at room temperature. In contrast to the behavior reported on Si(100), both the Auger measurements in this work on Si(111)-(7x7), and previous kinetic uptake measurements [32], indicated a reduced overall sticking efficiency for PH_3 adsorption on Si(111)-(7x7) at 300 K. The initial sticking coefficient, S_0, at 300 K, was determined to be 0.26 based upon uptake measurements [32]. HREELS measurements at 300 K clearly indicate a PH_3 dissociative adsorption process on Si(111)-(7x7) producing Si-H on the surface.

IV. Summary

We provide vibrational spectroscopic evidence for the dissociative adsorption of PH_3 on Si(111)-(7x7) at 80 K. The Si-H species is observed to be produced upon PH_3 adsorption. Depending upon the surface coverage, $PH_3(a)$ (minority species) and $PH_2(a)$ species are found on surface. The thermal dissociation of the surface PH_2 species occurs between 450 and 500 K, resulting in the capture of additional hydrogen and phosphorus on the surface.

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V. Acknowledgement

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Figure Captions

Figure 1. HREEL spectra from (a) clean and (b) - (e) PH_3-exposed Si(111)-(7x7) surface at 80 K. The PH_3 exposures were as follows (in units of PH_3 molecules/cm^2): (b) $5x10^{13}$, (c) $1x10^{14}$, (d) $1x10^{15}$ and (e) $2x10^{15}$.

Figure 2. Thermal desorption spectra of all the desorbing species observed from PH_3/Si(111)-(7x7). The temperature ramp used in these studies was $dT/dt = 1.6$ K sec^{-1}. Comparision of the integrated area of the PH_3 desorption trace to that of H_2 suggests that the observed $PH_3(g)$ corresponds only to a small fraction of a monolayer.

Figure 3. HREEL spectra of PH_3/Si(111)-(7x7) at 80 K after heating to various temperatures and cooling to 80 K. The initial saturation exposure of PH_3 was $2x10^{15}$ PH_3 molecules/cm^2.

Table I

Partial listing of the vibrational frequencies (cm^{-1}) of PH_3 and PH_x containing compounds - comparison with PH_3-derived species on Si(111).

PH_3		$PH_3(g)$[a]	$PH_3/Pt(111)$[b]		
	$\nu_s(PH_3)$	2328 cm^{-1}	2325 cm^{-1}		
	$\nu_d(PH_3)$	2323	2325		
	$\delta_s(PH_3)$	991	985		
	$\delta_d(PH_3)$	1121	1080		
	$\nu(PtP)$	--	370		

$- PH_2$		H_3SiPH_2[c]	P_2H_4[c]	CH_3PH_2[c]	$Si_2H_5PH_2$[d]
	$\nu_s(PH_2)$	2310 cm^{-1}	2312 cm^{-1}	2310 cm^{-1}	2300 cm^{-1}
	$\delta(PH_2)$	1069	1081	1093	1073
	$\nu(SiP)$	454	--	--	475-515

$\geq PH$		$(CH_3)_2PH$[e]	F_2PH[f]	$(CF_3)_2PH$[g]	$(CF_3S)_2PH$[g]
	$\nu(PH)$	2289 cm^{-1}	2240 cm^{-1}	2300 cm^{-1}	2320 cm^{-1}
	$\delta(PH)$	998	1016	850	894

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PH		R_1R_2PH[h] (7 compounds)

	$\nu(PH)$	2280-2290 cm^{-1}
	$\delta(PH)$	886-897 cm^{-1}

Si-PH$_2$		$PH_2 + PH_3$(minor) / Si(111)[i]

	$\nu(PH_2)$	2260 cm^{-1}
	$\delta(PH_2)$	1050
	$\nu(SiP)$	495

	$\nu(SiH)$	2070
	$\delta(SiH)$	630

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a ref. [31]

b ref. [23]

c ref. [25]

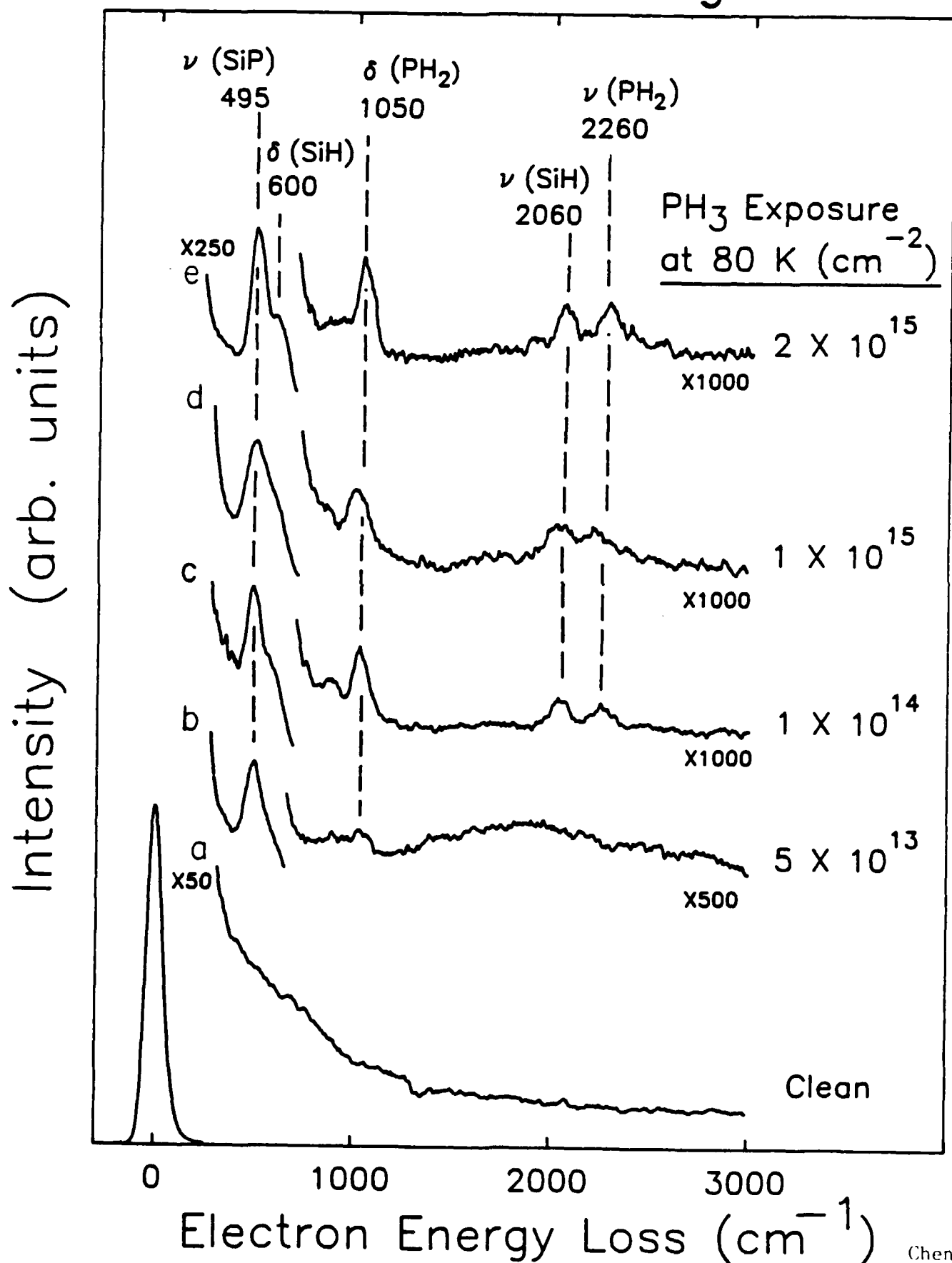d ref. [26]

e ref. [27]

f ref. [28]

g ref. [29]

h ref. [30]:   here R_1 = substituted Ph group; R_2 = Ph group
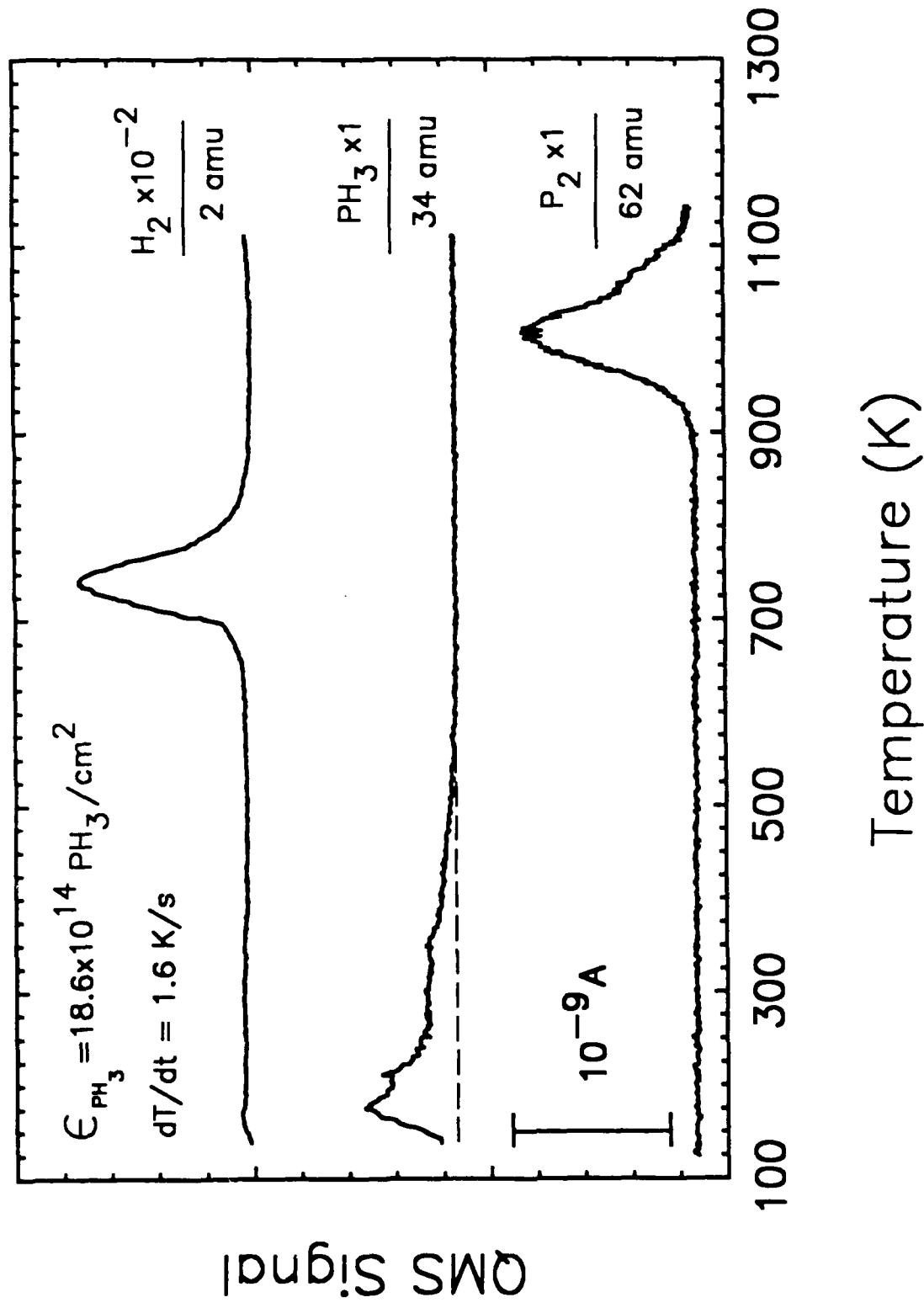
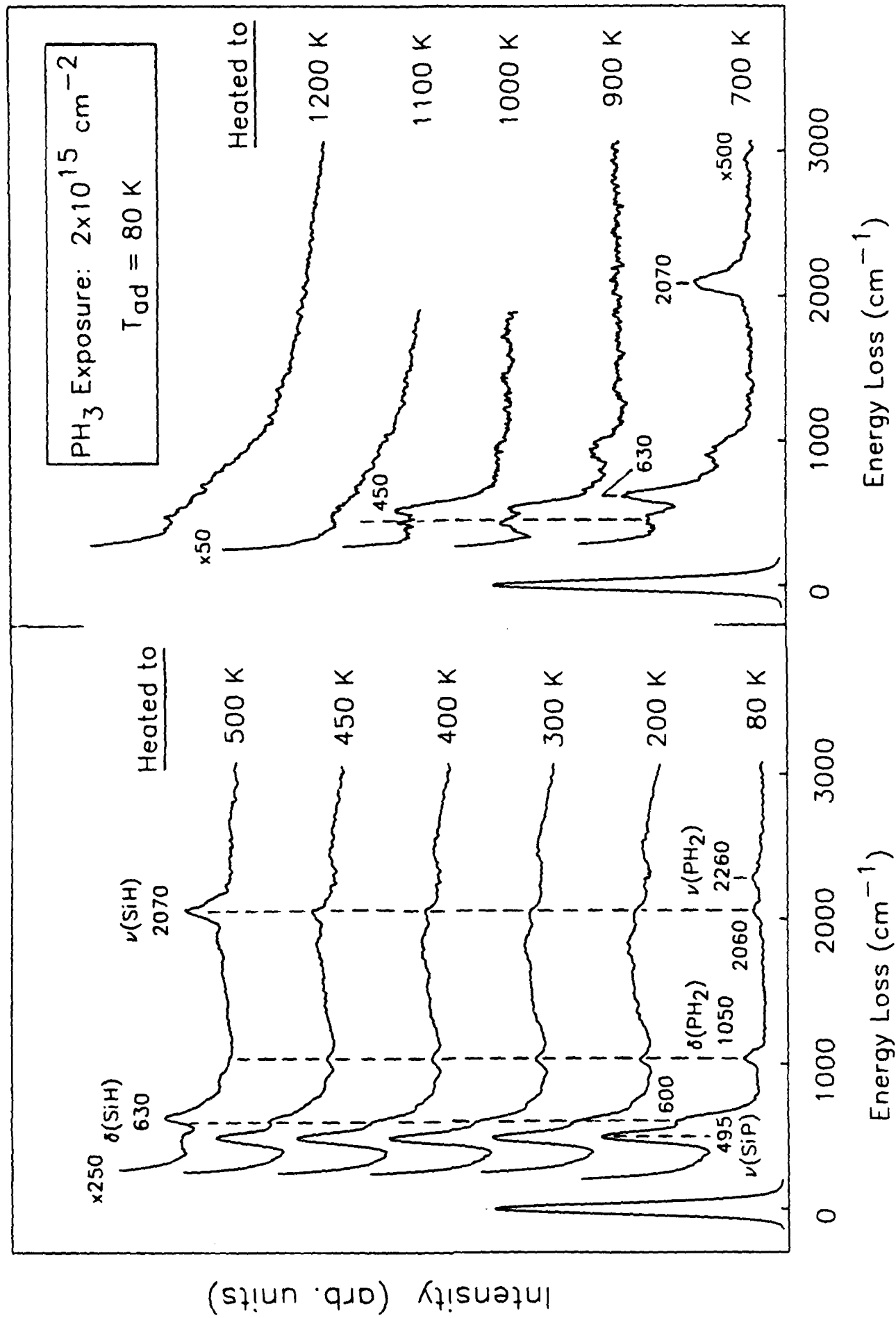i this work

HREEL Spectra of PH$_3$/Si(111) at Various Coverages

Thermal Desorption from $PH_3/Si(111)-(7\times7)$

$\epsilon_{PH_3} = 18.6\times10^{14}\ PH_3/cm^2$

$dT/dt = 1.6\ K/s$

$\frac{H_2 \times 10^{-2}}{2\ amu}$

$\frac{PH_3 \times 1}{34\ amu}$

$\frac{P_2 \times 1}{62\ amu}$

$10^{-9}A$

QMS Signal

Temperature (K)

Thermal Decomposition Effects – PH$_3$/Si(111)

Chen, et al

Figure 3

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