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The Surface Chemistry of s-Triazine on Si(100)-2x1

by

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Abstract

The thermal decomposition of s-triazine (ST) on Si(100)-2x1 was studied with HREELS, UPS, XPS and TDS. Two adsorption states for ST on the surface were observed, which yielded desorption peaks at 180 and 235 K, respectively. In the second adsorption state, which is thermally stable up to 420 K, ST is likely to lie flat on the surface as indicated by the virtual absence of the asymmetric ring breathing mode at 145 meV in HREELS and by the relatively lower ST coverage (<0.3 L) at temperatures above 200 K. Annealing a 1.2 L ST dosed sample at 550 K caused the dissociation of ST into HC=N. Meanwhile, NH and Si-H bonds were formed. Further annealing the surface at 780 K dissociated the CN-containing species and the NH bond. Above 800 K, a mixture of Si nitride and Si carbide was formed on the surface following the cracking of the CH bond and the desorption of the H species. The photodissociation of ST on Si(100)-2x1 was also examined; CN radicals in addition to the HCN species could be identified on the surface after it was exposed to 308-nm excimer laser radiation at 100 K.

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I. Introduction

Spectroscopic studies of s-triazine (ST), especially those of photoelectron and IR/Raman spectroscopy, have been reported by several groups,¹⁻⁷ because ST has high symmetry and serves as a model for its family of compounds. Photodissociation of ST was also studied, e.g., by Goates et al.⁸ using 193 nm laser and by Schrems et al.⁹ using a high-pressure Hg lamp. In these cases, ST photodecomposed into three HCN molecules, and noncyclic HCN trimers, respectively. The photodissociation of ST adsorbed on Ag at 514.5 nm, however, led to the formation of graphitic carbon.¹⁰

Fewer studies were carried out for the thermal reaction of ST on surfaces. Kordesch et al.¹¹ studied the thermal decomposition of ST on Pd(100) and Pd(111) using HREELS and TPD methods and the results were compared with those of other CN-containing compounds on the same surfaces. In the case of ST on Pt(111), a desorption peak at 740 K for C₂N₂ (m/e=56) was observed by Kingsley et al.¹².

In this article, we report the results of the surface reaction of ST on Si(100)-2x1 as studied by HREELS, UPS, XPS and TDS. The results are compared with those of other CN-containing molecules on Si surfaces studied recently in this laboratory, e.g., HCN on Si(100)¹³, HCN on Si(111)¹⁴, C₂N₂ on Si(100) and Si(111)¹⁵ and formamide on Si(100)¹⁶. The photodissociation of ST on Si(100) at 308 nm was also investigated in the present study and the results are compared with those of the thermal decomposition process.

II. Experimental

The experiment was carried out in a custom-designed UHV system with a base pressure of $\sim 6 \times 10^{-11}$ torr as described elsewhere.¹⁷ A single crystal Si(100) wafer from Virginia Semiconductor Corp. was cut into 1.0 x 1.5 cm samples. Before being

introduced into the UHV chamber, the samples were chemically cleaned with 5% hot HF solution. Further cleaning of the samples was done by annealing the surface at $T_s \geq 1500$ K repeatedly until no C, N and O could be detected by AES, XPS and/or HREELS. The Si(100) sample prepared in this way showed a sharp 2x1 LEED pattern and an intense peak at 0.8 eV below E_F due to the surface states in He(I) UP spectrum. The XP spectra were recorded using a Mg X-ray source with the pass energy set at $\Delta E = 50$ eV. He(II) photon beams ($E_0 = 40.8$ eV) were used for recording the UP spectra. In the HREELS measurement, an electron beam with a primary energy of 5 eV and a resolution of 6 meV for the full width at half maximum (FWHM) in the straight-through mode was utilized as the beam source. The FWHM and the beam intensity after scattering from a clean Si(100)-2x1 surface at 100 K are typically 9-10 meV and $\sim 4 \times 10^5$ counts/s, respectively. A Lambda Physik excimer laser (EMG-102) was employed for the photodissociation study. The laser was operated at 308-nm wavelength with a repetition rate of 5 Hz. The photon beam covered the whole surface area and the laser fluence was ~ 20 mJ/cm² · pulse.

The ST sample (97% pure from Aldrich Chemical Co.) was further purified by pumping it at dry-ice temperature with a diffusion pump. The vapor over the ST crystal at 300 K was used for the experiment. After purging the dosing line repeatedly, the ST sample was introduced into the UHV chamber through a 1.6 mm-diameter stainless steel tube and the ST dosages were estimated according to ion gauge reading.

III. Results

Figure 1 shows the HREEL spectra of 1.2 L ST on Si(100)-2x1 at 100 K taken at specular and 10° off-specular angles, respectively. In the specular spectrum, peaks at 50, 82, 113, 145, 163 (weak), 192 and 372 meV were observed. By analogy to IR/Raman results for the gas, liquid and solid ST^{6,7}, we attribute these peaks to

molecular vibrations as listed in Table 1 together with the strong IR/Raman peaks. In addition, a small hump at ~258 meV is likely the combination of the 113 and 145 meV modes. The 113 meV peak became more intense in the off-specular spectrum, and thus cannot be due to the combinations of the lower frequency vibrations. This peak is attributable to the symmetric ring breathing and CH wagging vibrations, which were red-shifted by about 10 meV upon the adsorption on Si(100)-2x1. The weak 163 meV peak, whose relative intensity was also stronger in the off-specular spectrum, is due to one of the ring modes observed at 175 meV in IR/Raman spectra and possibly the combination of the 50 and 113 meV modes.

The thermal effect on the HREELS of 1.2 L ST dosed Si(100) is illustrated in Fig. 2. As the sample was warmed to 200 K, the 145 meV peak was attenuated and the 258 meV hump diminished. Annealing the sample at 420 K caused a further decrease of the 145 meV peak and the appearance of a strong peak at 58 meV in the spectrum. At 550 K, all the ring vibrational modes virtually vanished indicating the breaking of the ring structure of the triazine molecule. Meanwhile, the formation of the SiH and NH bonds is evidenced by the appearance of new peaks at 255 and 420 meV. These two peaks are due to the Si-H and NH stretching vibrations, respectively. Furthermore, the new and intense peak at 70 meV is from the Si-N and Si-C stretching vibrations, while the CH stretching vibration component, at ~380 meV, may be attributed to the formation of HCN species. The corresponding HC=N stretching and HCN deformation modes at 190 and ~80 meV, respectively, are also visible in the spectrum. After the sample was annealed at 780 K, the HREEL spectrum was dominated by the peaks at 90, 255 and 364 meV due to the Si-N and Si-CH_x, Si-H and CH stretching vibrations, respectively. Finally, at 1000 K, the breaking of the CH bond and the desorption of the H-species were indicated by the disappearance of the 255 and 364 meV peaks and the shift of the 90 meV peak to 100 meV.

Shown in Fig. 3 are the He(II) UP spectra taken from ST on Si(100)-2x1 dosed at 100 K and then annealed at the indicated temperatures. As 0.3 L ST was dosed on the surface at 100 K, peaks at 3.9, 5.4, 8.2, 10.5 and 15.5 eV below E_F were observed. Further dosing of the ST caused the shift of these peaks toward higher binding energies. After the surface was exposed to 2.0 L ST, these peaks appeared at 4.6, 5.9, 9.1, 12.3 and 16.2, respectively. In addition, a weak peak at 7.4 eV became evident in the UP spectrum. The corresponding peak at 13.25 eV in the gaseous ST UP spectrum was also noted to be comparatively weak.² The assignments for the UP spectrum of the gaseous ST by several groups have apparently shown some minor contradictions.¹⁻⁵ However, our ab initio MO calculation at the Hartree-Fock (HF) level of theory, which is fully consistent in energy levels with the recent ab initio calculation by Walker et al.,¹ allows us to assign the observed peaks as shown in Table 2. After the 2 L ST dosed Si(100) sample was annealed at 200 K, the UP spectrum is virtually identical to that of 0.3 L ST dosed Si(100) at 100 K. Further annealing the surface at 420 K caused no obvious changes in the spectrum. In contrast, when the sample was annealed at 550 K, most of the molecular features diminished, consistent with the HREELS result mentioned above. Meanwhile, new peaks at 6.7 and 12.8 eV dominated the spectrum. The 6.7 eV peak is attributable to the Si-N and Si-C bonds, while that of the 12.8 eV is due to the N-H bond. Furthermore, the 4 eV peak is shifted to 4.2 eV, which has contributions from the Si-H species. At 800 K, the 4.2 and 12.8 eV peaks vanished because of the desorption of the H species and the breaking of the N-H bond. The remaining broad peak at ~6.4 eV is due to the formation of Si carbide and Si nitride.

The accompanying N_{1s} and C_{1s} XP spectra were shown in Figs. 4a and 4b, respectively. After the Si(100) surface was exposed to 0.5 and 2 L ST at 100 K, peaks at 401.2 and, 288.0 eV were noted for N_{1s} and C_{1s} photoelectrons. When the 2 L ST

dosed Si(100) was warmed to 200 K, both N_{1s} and C_{1s} peak intensities attenuated significantly indicating a partial desorption of the adsorbate. In addition, the C_{1s} peak broadened somewhat and the N_{1s} peak shifted to lower binding energy by -0.8 eV. Annealing the sample at 420 K caused no obvious XPS changes except a slight shift of both N_{1s} and C_{1s} peaks toward lower binding energy. However, further annealing the surface at 550 and 800 K caused a further shift of the N_{1s} peak to 397.8 and 397.2 eV, respectively, while the C_{1s} XP spectra became too weak to give any conclusive information. Nevertheless, the spectra were noted to have more and more contributions from the lower B.E. components at 550 and 800 K.

Figure 5 shows the TDS of ST ($m/e = 81$) on Si(100) dosed at 100 K and heated at a rate of ~ 2 K/s. The corresponding HCN ($m/e = 27$) and NH₃ ($m/e = 17$) TD spectra from 3.0 L and 1.0 L ST dosed Si(100) are also shown in the figure. For the ST species, two peaks at 180 and 325 K were observed and the first peak became more intense and shifted to lower temperatures as the ST dosage was increased. The TDS of HCN is effectively the same as that of (HCN)₃, suggesting that the HCN⁺ signal derives from the fragmentation of the parent ion in RGA. No mass 17 for NH₃ was observed in the present study.

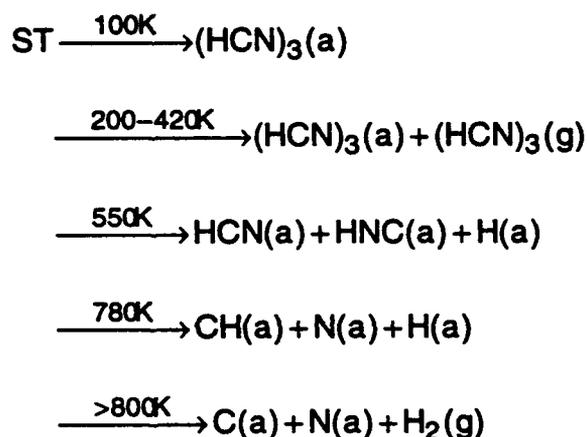
The 308-nm laser induced dissociation of ST adsorbed on Si(100) was also investigated and the HREELS results are presented in Fig. 6. After a 1 L ST dosed Si(100) sample was exposed to 308-nm laser beam with a fluence of ~ 20 mJ/cm²-pulse, operating at a repetition rate of 5 Hz for 5 min, the 145 meV peak due to the asymmetric ring breathing and CH rocking vibrations were attenuated noticeably. In addition, a new peak at 220 meV appeared in the spectrum. These changes became more obvious as the surface was irradiated with the laser for an additional 20 min. Further laser irradiation (60 min total) caused the disappearance of

all molecular vibrations and the HREEL spectrum was dominated by the peaks at 62, 82, 195, 220 and 364 meV.

IV. Discussion

1. Thermal decomposition

Based on the UPS, XPS, TDS and HREELS results presented in the preceding section, the thermal dissociation of ST on Si(100)-2x1 can be briefly summarized as follows:



The molecular adsorption of ST on Si(100) at 100 K was clearly identified by both HREELS and UPS. The vibrational peaks compare closely with those observed in Raman/IR spectra taken from liquid, gaseous or solid ST samples (Table 1). The peaks observed in HREELS correspond to the strong or at least medium strong ones in the Raman spectrum of the liquid ST, because ST is a highly symmetric molecule. In the corresponding off-specular HREEL spectrum, the peaks at 113 and 372 meV from the symmetric ring-breathing or CH wagging and the CH symmetric stretching modes, respectively, became the dominant features, probably because no dipole change was involved in these vibrations. In the UP spectrum, six peaks were noted when the surface was exposed to 2 L ST at 100 K. These peaks match well with those

reported for the gaseous ST UPS results. After the sample was warmed to 200 K, all peak intensities attenuated and the 7.4 eV peak was hardly visible due to the partial desorption of the adsorbate. In addition, the peaks shifted to lower binding energies by about 1 eV. The peak shifting may be caused partially by the intermolecular interaction at higher dosages. On the other hand, it may indicate a different adsorption state for ST on Si(100) at lower dosages (or after warming the sample to 200 K). The different adsorption states were unambiguously shown in the TD spectrum, where two peaks at 180 and 325 K were observed for the parent molecules.

The second adsorption state of ST on Si(100) is also indicated by the HREEL spectrum. After warming the sample to 200 K, no obvious changes were noted except a decrease of the 145 meV peak due to the asymmetric ring-breathing and/or the CH rocking modes. This observation suggests that the molecule lies flat on the surface for the second adsorption state, thus the contribution from the ring-breathing mode becomes weaker because of the absence of the perpendicular dipole change. This argument seems to be reasonable, particularly when considering the fact that this mode was mainly due to the dipole scattering before warming the surface to 200 K (see Fig. 1). Under higher dosage conditions, some or most of the ST molecules probably adsorbed vertically on the surface, resulting from insufficient surface sites. The interaction between the surface and the stand-up ST would be weaker and a lower desorption peak would be expected to appear in TDS. Indeed, as alluded to above, a desorption peak at 180 K in addition to that at 325 K was observed and the peak intensity increased with increasing of the ST dosage. Other supporting evidence for the parallel (flat) adsorption of ST on Si(100) at 200 K is the relatively low coverage of ST left on the surface as indicated in the N_{1s}, C_{1s} XP and UP spectra. The N_{1s} and C_{1s} XPS signal intensities are less than 50% of those taken from 0.5 L-dosed sample and the UPS signals are slightly weaker than those taken from a 0.3 L-dosed sample.

These observations suggest that the remaining adsorbate at 200 K is less than 0.25 L, a reasonable value for one monolayer ST parallelly adsorbed on Si(100)-2x1, assuming that one ST molecule consumes two Si dimers in the same dimer row as depicted in Fig. 7. Such an adsorption geometry is further supported by the He(I) UPS measurement, which shows that exposing the surface to 0.3 L ST caused a virtual disappearance of the surface states originated from the Si dimers (Fig. 8).

Annealing the sample at 420 K induced a slight decrease of the 145 meV peak in HREELS, the N_{1s} and the C_{1s} photoelectron signals in XPS and the peak intensities in UPS, because of the further desorption of the adsorbate as evidenced by the desorption peak at 325 K in TDS (Fig. 5). However, all the molecular features persisted in HREELS and UPS, and there was no obvious peak shift in N_{1s} or C_{1s} XP spectra. Clearly, no appreciable dissociation of the adsorbate occurs at 420 K.

In contrast, annealing the surface at 550 K caused all molecular features to diminish in HREELS and UPS. Meanwhile, new peaks at 4.2, 6.7 and 12.6 eV due to Si-H, SiN and SiC and NH bonds, respectively, appeared in the UP spectrum. In HREELS, these new features could be related to the 255 (Si-H), the broad 70 (SiN and SiC) and the 420 meV (NH) peaks. The remaining peak at ~120 meV is attributable to the CH wagging and NH bending vibrations, while that at ~190 meV could be due to either HC=N stretching or the NH₂ deformation mode.²⁰ Since there is no NH₃ being observed in the TD spectrum (Fig. 5), we attribute the 190 meV peak to the HCN species. When adsorbed on other surfaces, HC=N also showed a peak at ~190 meV for the HC=N stretching mode. In addition, two other modes at 80 and 360-410 meV were reported for the HCN deformation and the CH stretching vibrations, respectively.^{13,14,18,19} In our HREEL spectrum, the CH stretching mode appeared at 380 meV, but the HCN deformation mode was not well resolved from the broad 70 meV peak. In the corresponding XPS measurement, the dissociation of the ST was

indicated by the N_{1s} peak shift from 399.9 to 397.8 eV and by the broadening of the C_{1s} peak, which became too weak to give any conclusive information above 550 K.

The formation of some NH-containing species as indicated by the 420 meV peak in HREELS and the 12.6 eV peak in UPS also occurred on the surface at this temperature.¹⁷ The NH-containing species could be in the form of HNC, HCNH or NH. For the first two cases, the corresponding C=N stretching vibration should be at 170 and 160 meV, respectively, and the peaks should be probably rather weak as these species are likely to adsorb parallelly on a Si(100) surface.^{13,14,16} Indeed, two humps around 160 and 170 meV are evident in the 550 K HREELS (Fig. 2). However, they are too weak to allow us to make a conclusive remark on the formation of HNC or HCNH species.

At 780 K, the peaks between 150 to 200 meV vanished and the HREEL spectrum was dominated by a peak at 90 meV due to the SiN and SiC stretching vibrations. In addition, two other peaks at 255 and 360 meV indicated that some H and CH species remained on the surface. On the other hand, the attenuation of the features between 150 and 200 meV indicated the dissociation of the C=N bonds. Further annealing the sample at higher temperatures caused the break of the CH bond and the desorption of the H species as evidenced by the disappearance of the 255 and 360 meV peaks in HREELS. The corresponding peaks at 12.8 and 4.3 eV due to the NH and Si-H bonds in the UP spectrum also vanished after the sample was annealed at 800 K.

2. Photodissociation at 308 nm

Pure or Ar-diluted ST has been reported to dissociate into vibrationally excited HCN at 193 nm with less than 1/40 of its yield being HNC.⁸ Similarly, it has been shown to photo-isomerize into linear HCN trimers, when ST was isolated in solid Ar

and irradiated with a high-pressure Hg lamp.⁹ In the present study, we examined the photodissociation of ST adsorbed on Si(100) at 100 K using 308-nm photon beams. The process was monitored with HREELS and the results are presented in Fig. 6. When a 1 L ST dosed Si(100) sample was exposed to 308 nm laser radiation, the dissociation of the adsorbate was indicated by the gradual disappearance of the HREELS peaks at 116 and 145 meV. The former peak is due to the symmetric ring-breathing and the CH wagging vibrations, while the latter peak is due to the asymmetric ring-breathing and the CH rocking modes. Meanwhile, the CH stretching peak at 360 meV became broader with more contributions from the higher frequency component. This higher frequency component is due to the formation of the HCN adspecies, which is also indicated by the relative intensity increase of the 80 and 190 meV peaks. As discussed above in the thermal decomposition section, three peaks at 80, 190 and 380 meV were observed when the ST-dosed Si(100) sample was annealed at 550 K and the peaks can be attributed to the HCN deformation, HC=N and CH stretching vibrations, respectively, for the HC=N adspecies.^{13,14} Thus, the observed changes in HREELS (Fig. 6) suggest that HCN was formed when the ST dosed sample was exposed to 308-nm laser radiation.

Furthermore, a new peak at 220 meV appeared in the HREEL spectrum and became more intense as the ST-dosed sample was exposed to the laser for a longer time. This peak, which was not observed in the thermal desorption process, is likely due to the CN radicals. The CN radicals are expected to give a higher CN stretching vibrational frequency than the HC=N does.^{13,14} On Pd(111) and Pd(100) surfaces, the CN stretching modes for CN and HCN adspecies were at 220-40 and ~190 meV, respectively.¹⁹

As to the photodissociation mechanism, i.e., whether the dissociation is induced by the excitation the adsorbate or the substrate, we do not have enough information to

provide a definitive conclusion. However, the additional product CN radical suggests that the laser induced surface heating is not likely to be a major factor in the present study. This argument is consistent with the fact that no obvious Si-H species was formed in the photoprocess, as in the thermal decomposition reaction described above. Other supporting evidence is that ST on Si(100) is thermally stable up to $T_s > 420$ K, which cannot be reached by the present low energy pulse laser excitation.

Energetically, the direct excitation of the adsorbate provides a more reasonable interpretation. When excited at 193 nm, the gaseous ST molecule photodissociated into vibrationally excited HCN fragments which may carry up to 36.2 kcal/mol excess energy. The 308-nm photon would also supply sufficient energy (92.8 kcal/mol) for ST to overcome the activation energy of 80.6 Kcal/mol²¹ for dissociation into 3HCN. If the adsorbed ST absorbs a 308-nm photon and also dissociates into 3HCN, then HCN will carry ~17.7 kcal/mol. excess energy. This energy may result in product desorption and dissociation into H and CN depending on the HCN adsorption geometry. Since the three HCN molecules have different bonding with the surface after the dissociation of the ST on Si(100)-2x1, various photoproducts could be formed on the surface as illustrated in Fig. 7.

The fact that CN was formed without the presence of the Si-H species is interesting. The H atom may be directly ejected out of the surface upon the dissociation of the HCN due to the formation of the strong Si-CN bond or indirectly desorb from the surface by the subsequent laser radiation. Previously, we have shown that 308-nm laser irradiation caused the partial dissociation of the NH bonds in N₂H₄ on Si accompanied by the pronounced desorption of the H species.¹⁷ Finally, it should be pointed out that photogenerated charge-carrier may also induce the dissociation of ST on Si(100). Further studies, e.g., using different wavelength photon

beams, are needed to gain a better understanding of the photochemistry of the ST on Si(100)-2x1.

Conclusion

The thermal- and photo-dissociation of s-triazine adsorbed on Si(100)-2x1 were studied with HREELS, UPS, XPS and TDS. Two desorption peaks at 180 and 325 K for the parent molecules were observed in TDS. The latter peak is likely due to the molecules parallelly adsorbed on the surface. Annealing the surface at 550 K caused the dissociation of ST. The HC=N, Si-H, and NH-containing adspecies and possibly some other C=N containing species, such as HC=NH and HNC, were produced. Further annealing the sample at 780 K led to the dissociation of the CN and the NH bonds. Above 1000 K, a mixture of Si carbide and Si nitride was formed on the surface.

When 308-nm photon beams were allowed to interact with the ST-dosed Si(100) at 100 K, the ST molecule photodissociated into HCN molecules, similarly to the gaseous ST photodecomposition process at 193 nm. However, CN radicals were also formed on the surface in the present study as indicated by the 220 meV peak in HREELS. No similar peak was observed in the thermal decomposition of ST on Si(100). This suggests that the photodissociation mechanism differs somewhat from that of the thermal reaction.

Acknowledgment

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Table 1. Vibrational frequencies of s-triazine

Mode	Raman ^(a)		HREELS ^(b) on Pd(100) at 120 K	HREELS ^(c) on Si(100)-2x1
	Solid	Liq.		
ring	42	42	45	50
ring	84	84	89	82
ring-breathing (sym.)	124	123		113
CH wag	128			
ring-breathing (asym.)	139	140	134	
CH rocking	146	146		145
ring	175	175	175	163
ring	192	193	191	192
CH stretching	377	377	377	372

(a). Ref. 6; (b) Ref. 11; (c). This work.

Table 2. The bands in photoelectron spectra of s-triazine

Gaseous ^(a)	On Si(100) ^(b)	Orbitals
10.01	4.6 (10.3)*	6e'
11.69	5.9 (11.6)	1e"
13.26	7.4 (13.1)	5a'1
14.56	9.1 (14.8)	1a"2+5e'1
17.1 18.05	12.3 (18.0)	1a'2
21.0	16.2 (21.9)	4e'

* A value of 5.7 eV was added for the correction of work function and the relaxation energy upon the adsorption.

(a). Ref. 2; (b) This work.

Figure Captions:

1. HREEL spectra for 1.2 L s-triazine on Si(100)-2x1 taken at specular and 10° off-specular angles, respectively.
2. HREEL spectra for 1.2 L s-triazine on Si(100)-2x1 dosed at 100 K and annealed at the indicated temperatures. All spectra were recorded at specular angle. (The figure has been separated as a and b for visual clarity.)
3. He(II) UP spectra for s-triazine on Si(100)-2x1 dosed at 100 K and annealed at the indicated temperatures.
4. N_{1S} (a) and C_{1S} (b) XP spectra for s-triazine on Si(100)-2x1 dosed at 100 K and annealed at the indicated temperatures.
5. TD spectra for (HCN)₃ (m/e=81), HCN (m/e = 27) and NH₃ (m/e = 17) taken from s-triazine on Si(100)-2x1. The surface was exposed to the indicated amount of s-triazine at 100 K and heated at a rate of 2 K/s.
6. HREEL spectra for s-triazine on Si(100)-2x1 after the sample was irradiated with 308-nm laser for the indicated times at 100 K.
7. The geometry of s-triazine adsorbed parallel on Si(100)-2x1 (a) and HCN on Si(100) after photodissociation. Note that the three HCN have different adsorption geometries.
8. He(I) UP spectra for s-triazine on Si(100)-2x1 showing the attenuation of surface states peak (0.8 eV) upon the adsorption of s-triazine.

Fig. 1

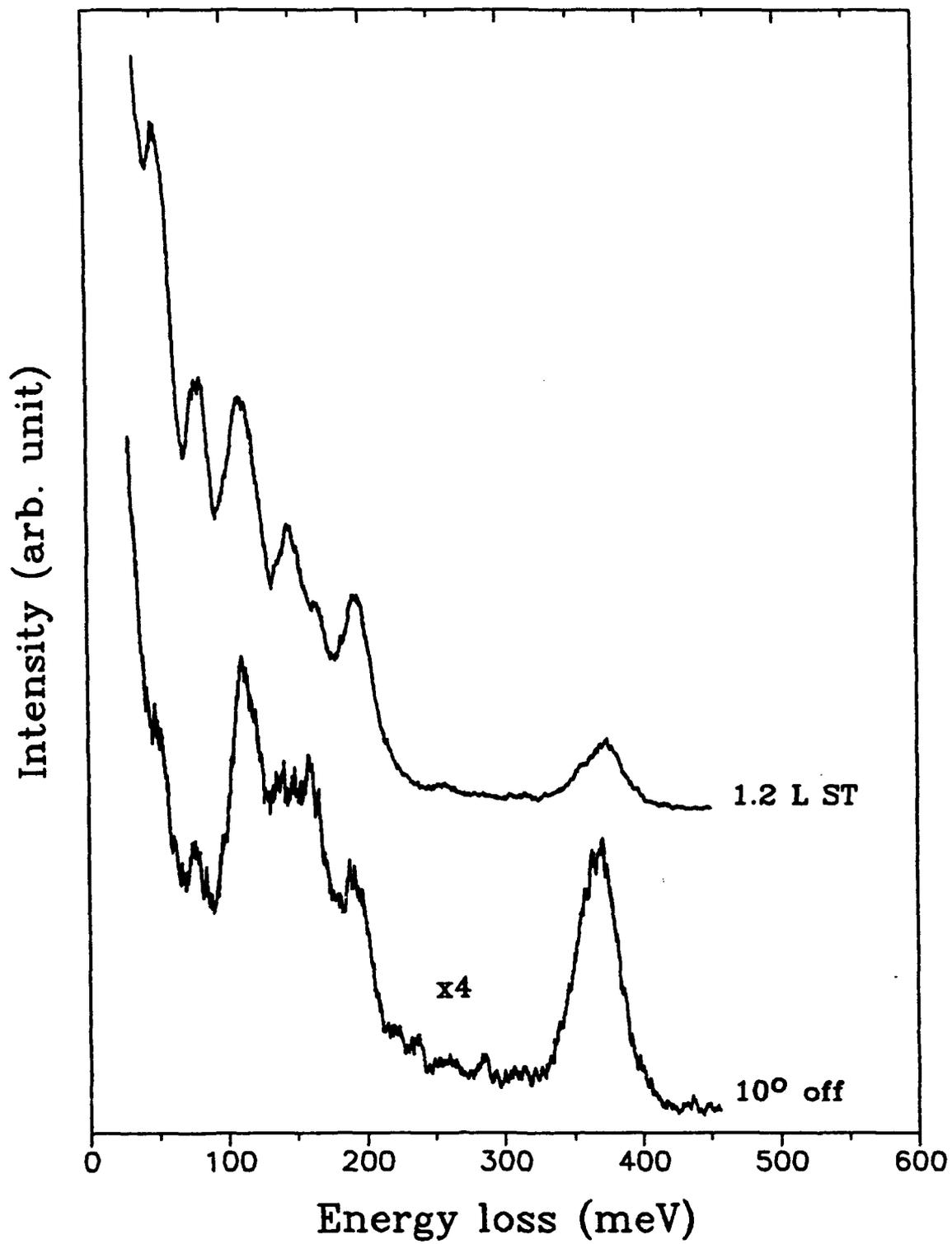
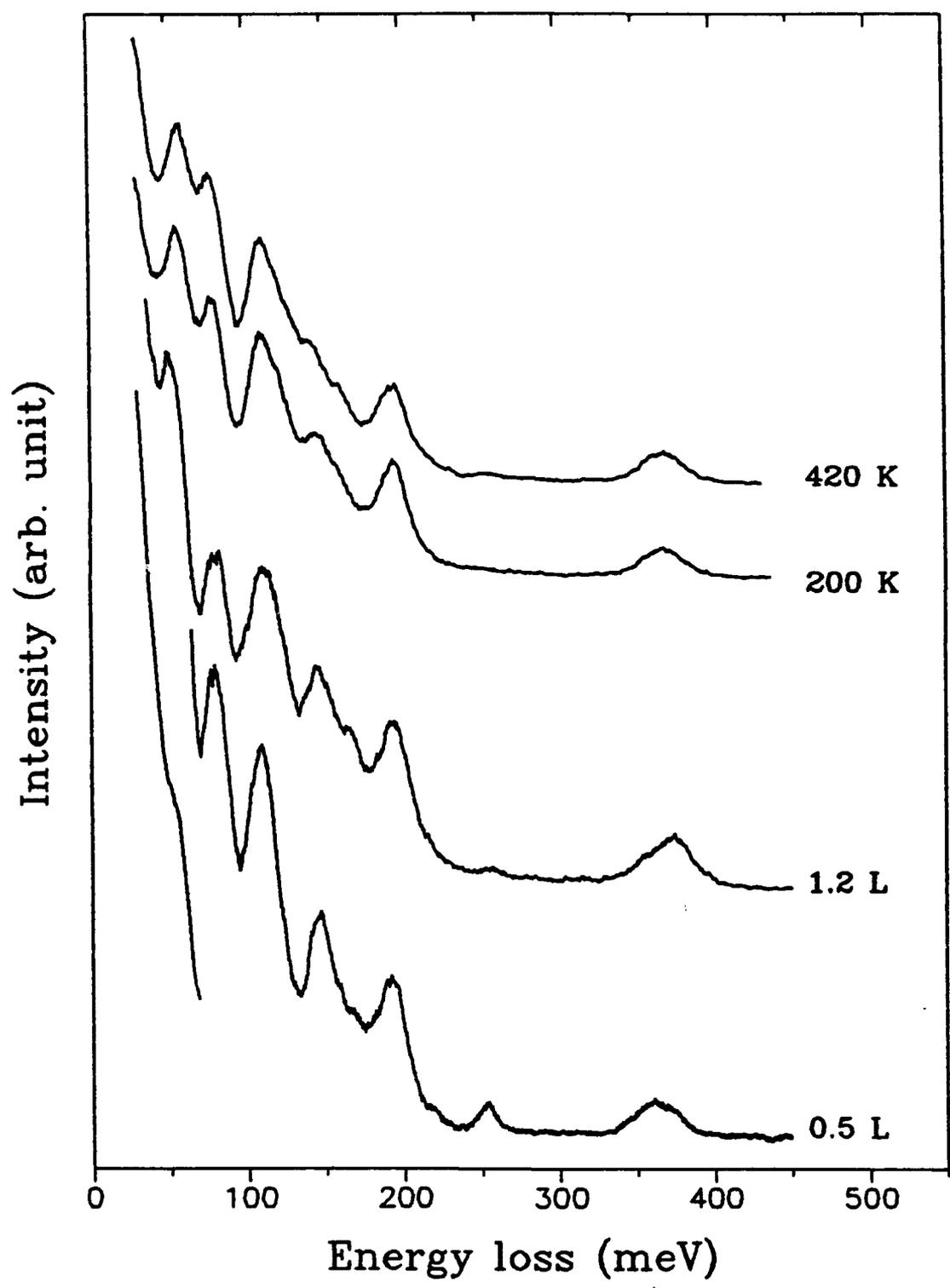


Fig. 2a



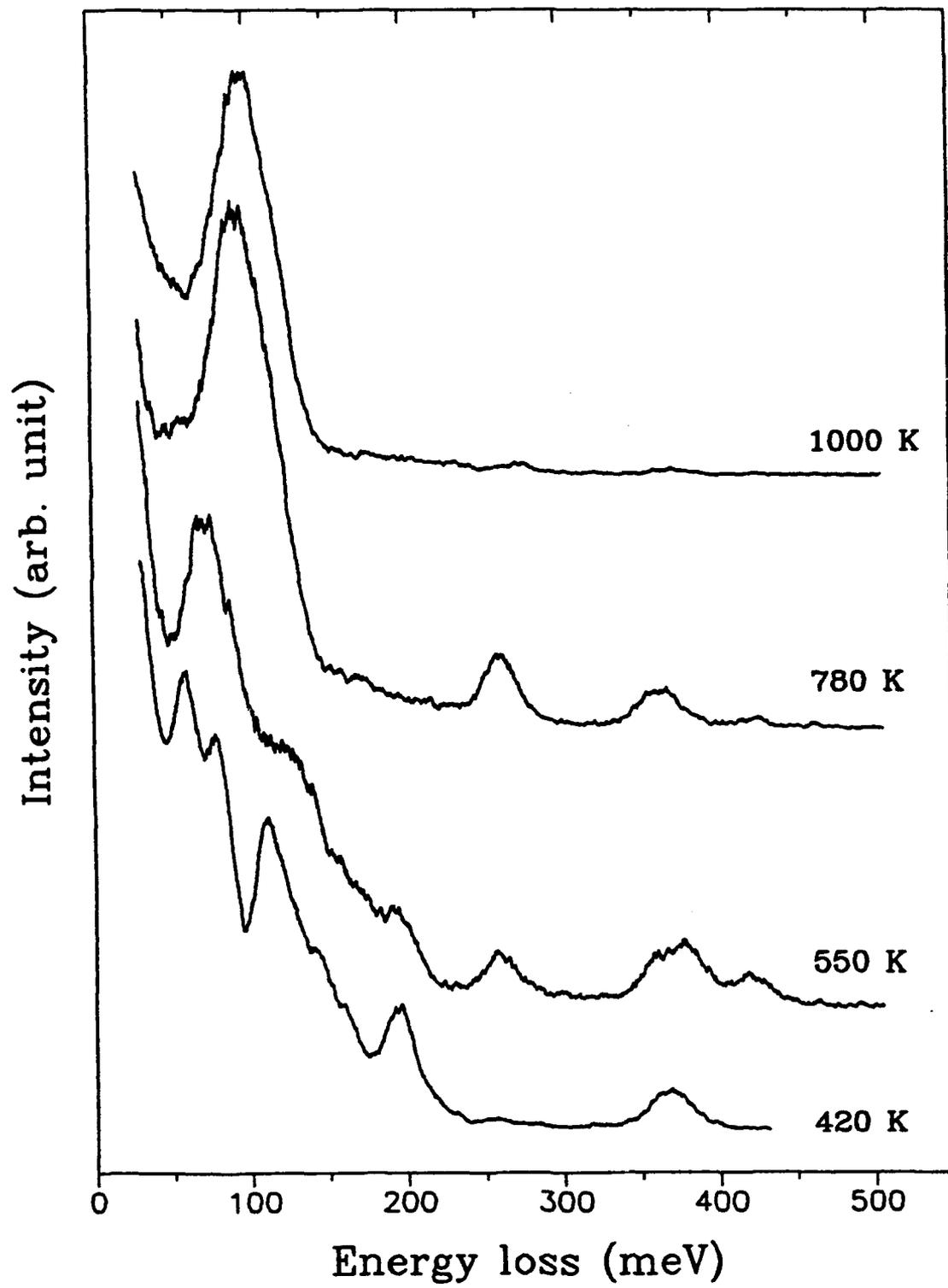


Fig. 3

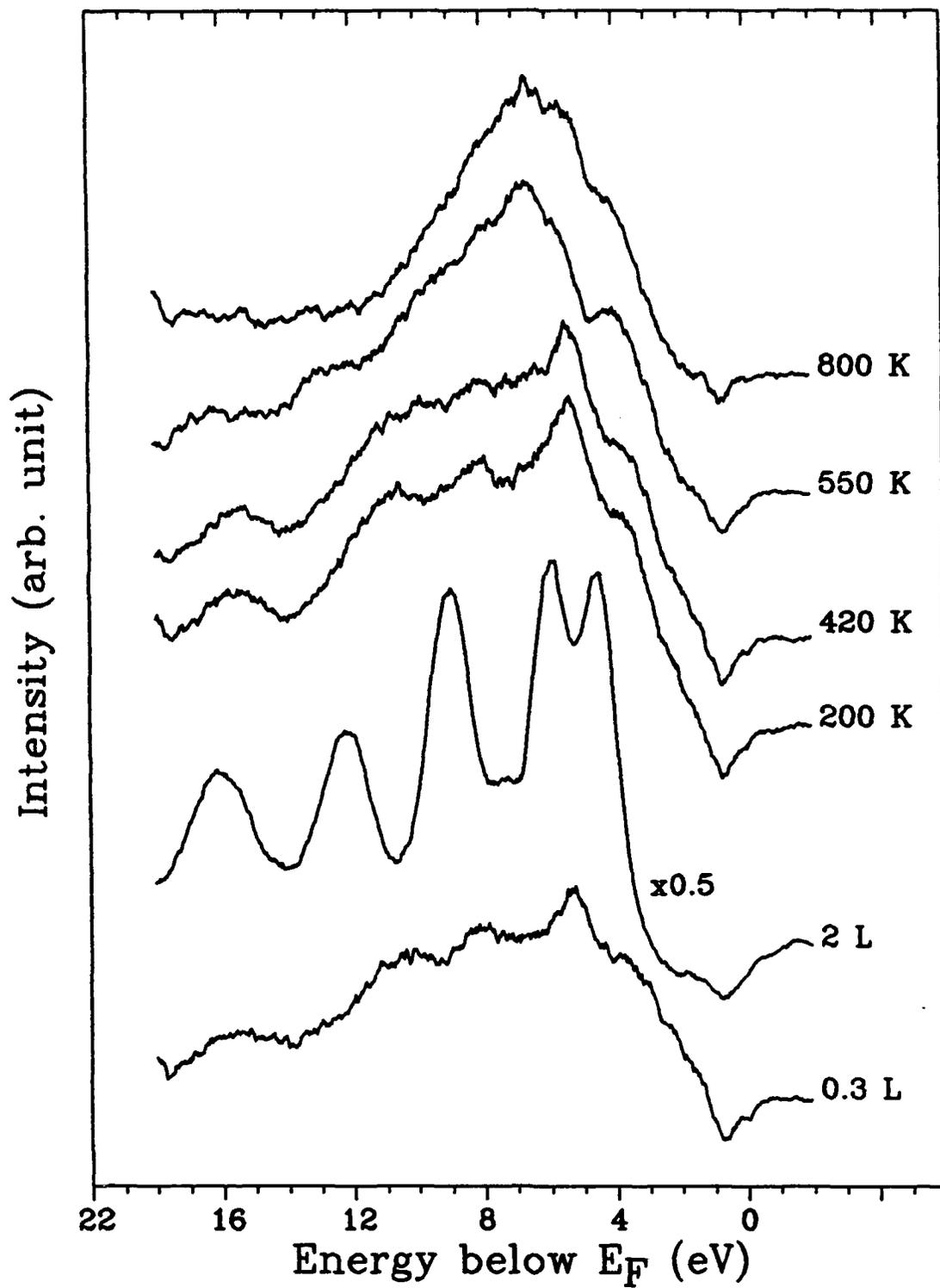


Fig. 4a

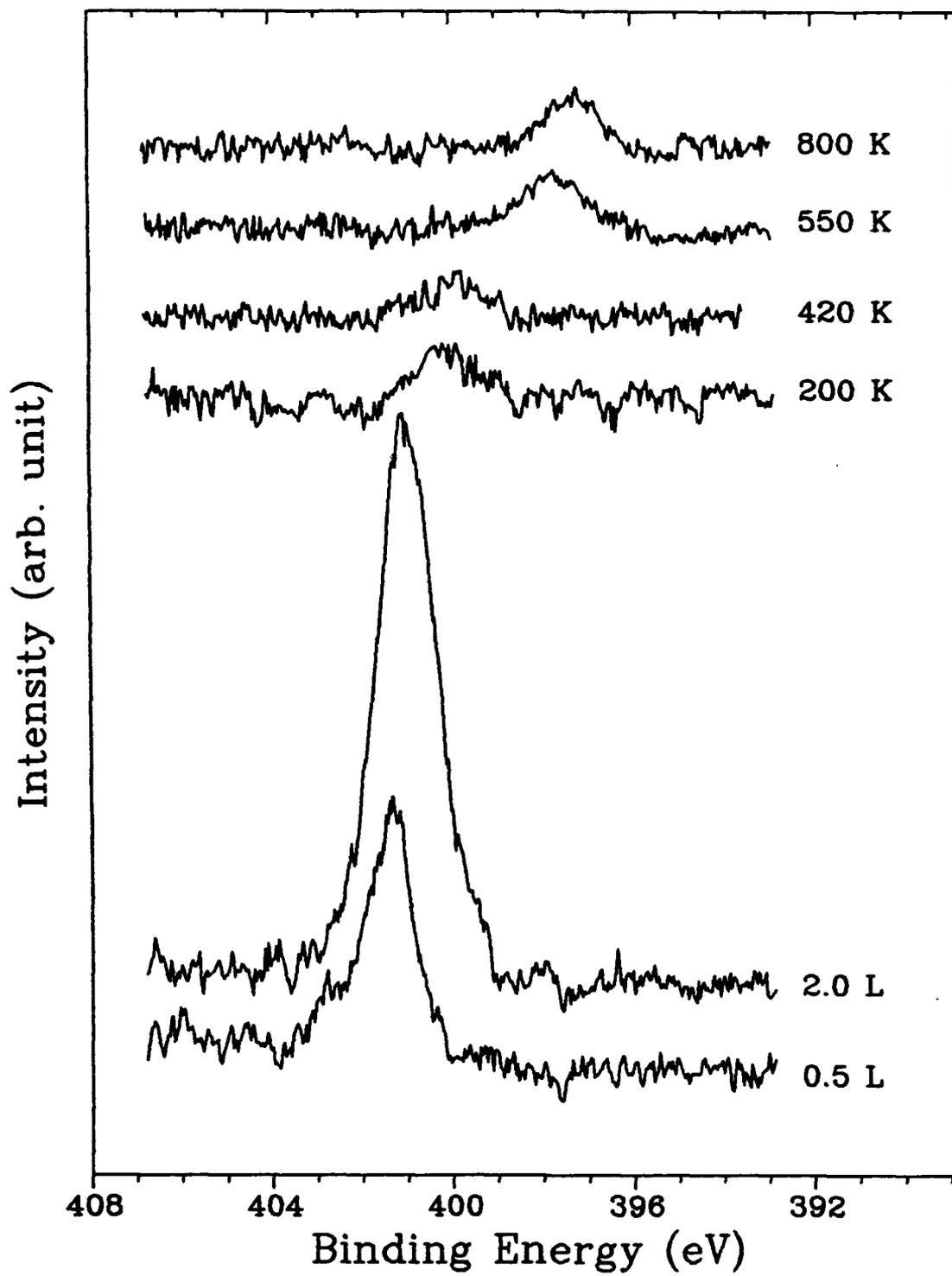
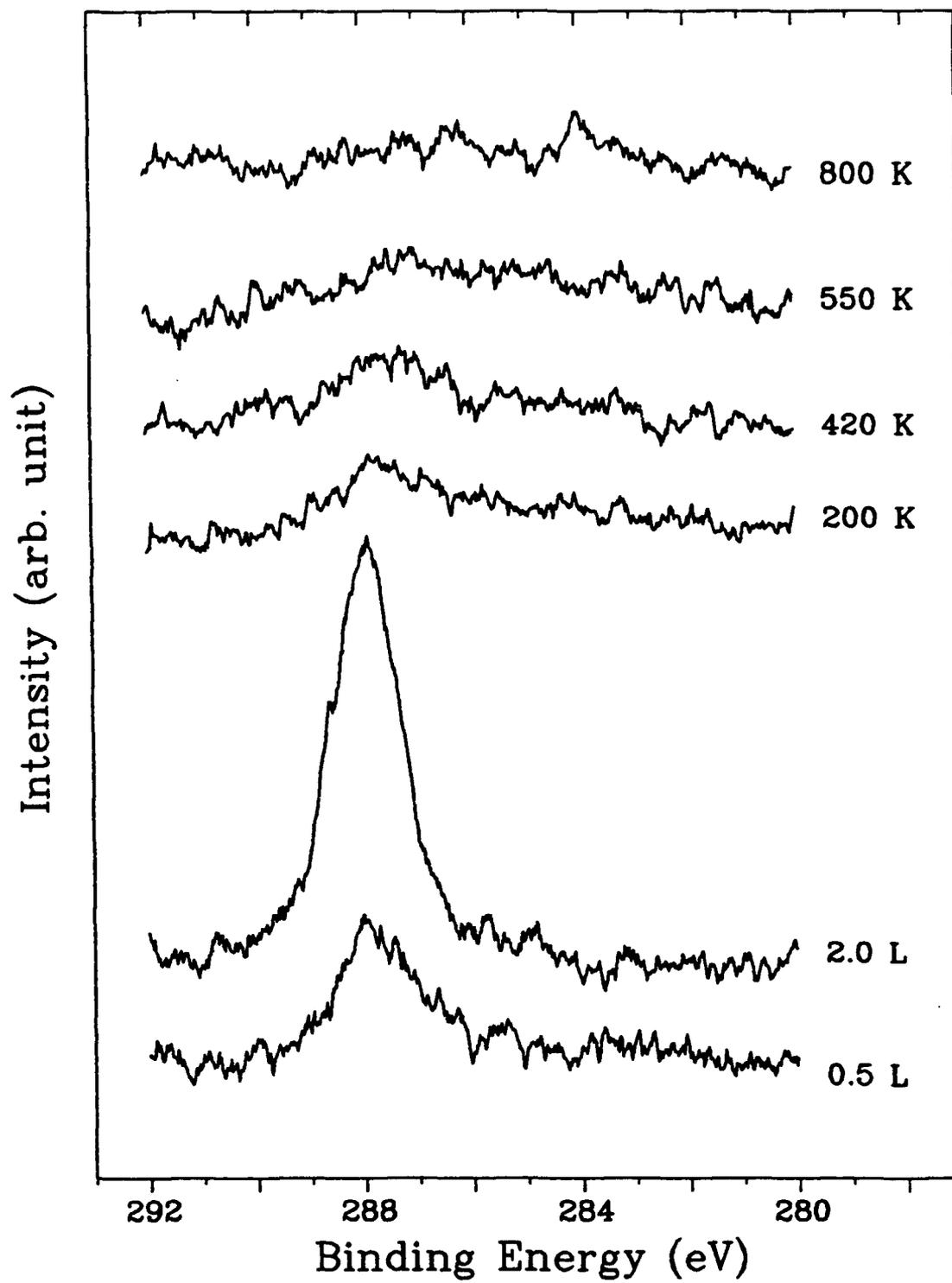
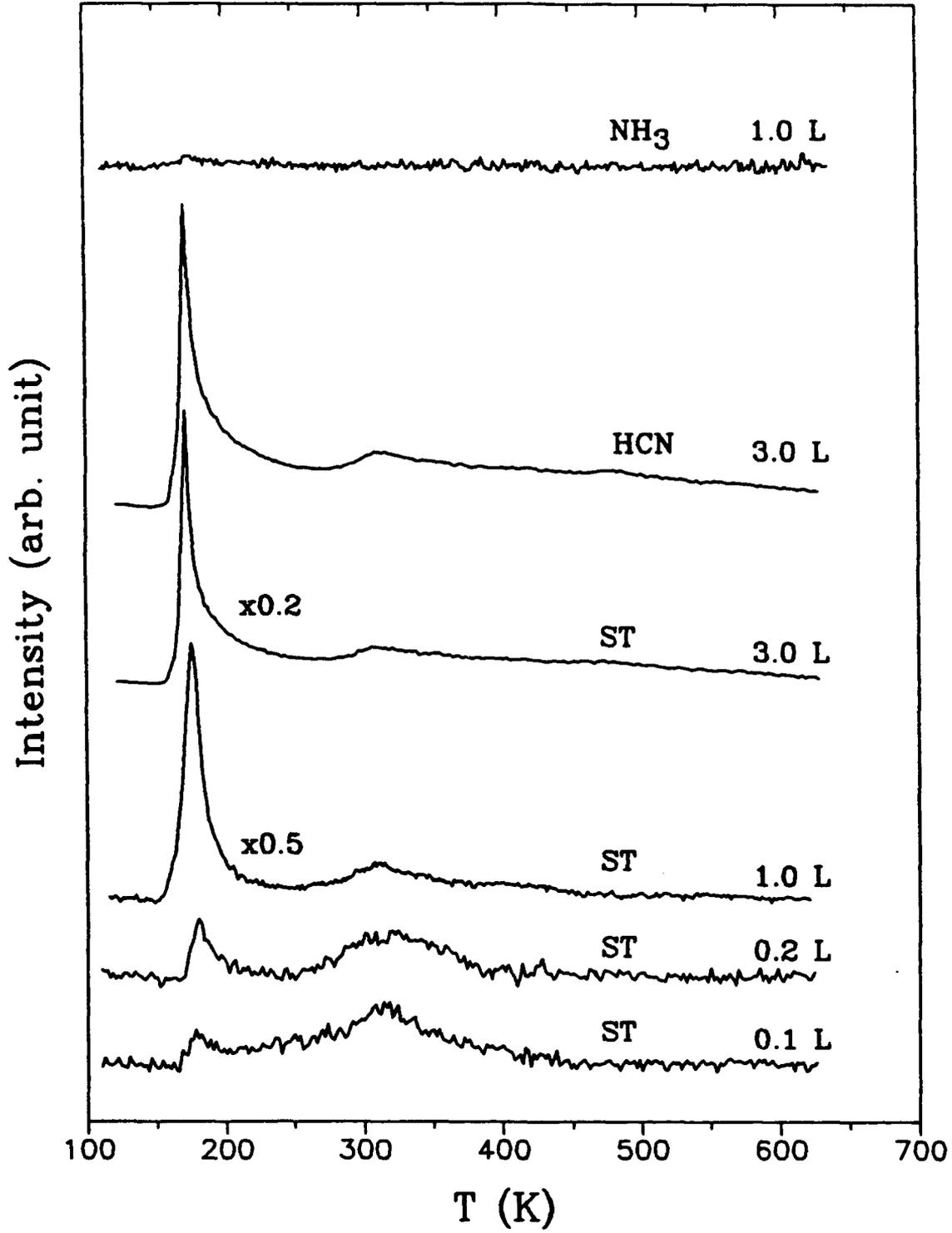
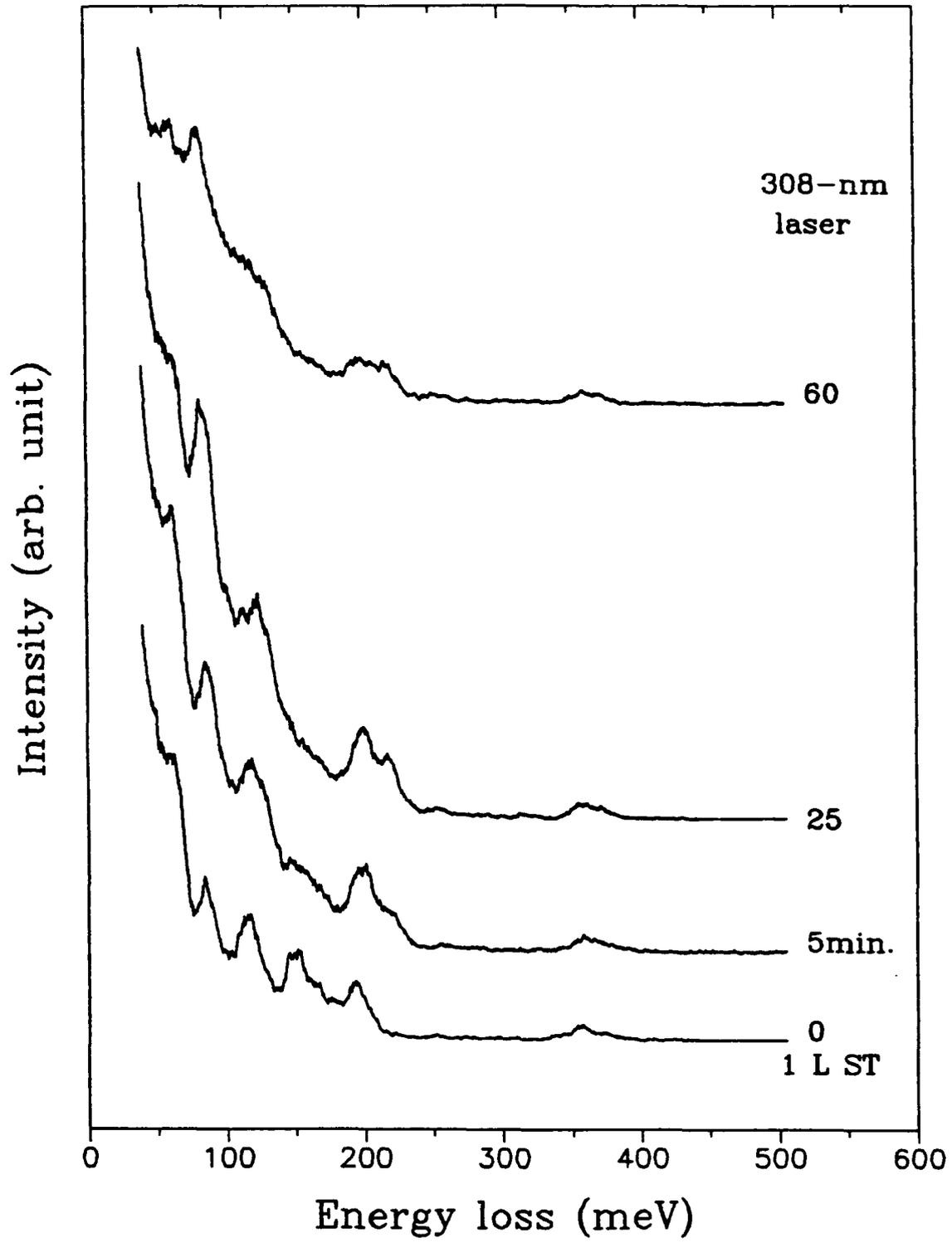


Fig. 4b







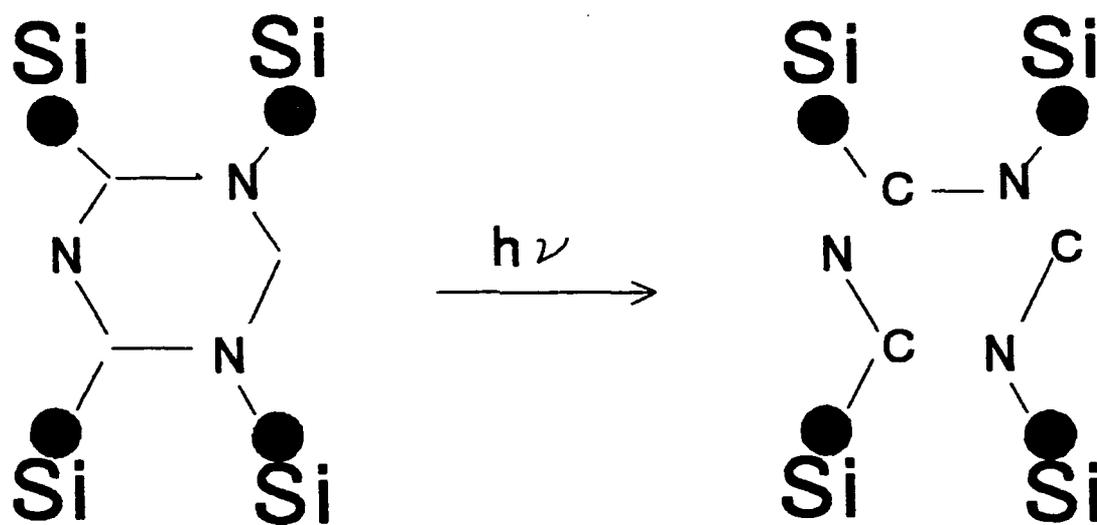


Fig. 8

