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Publication Date

1991-10-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Accelerator & Fusion Research Division

Presented at the Seventh International Conference on Synchrotron Radiation
Instrumentation, Baton Rouge, LA, October 28-31, 1991,
and to be published in the Proceedings

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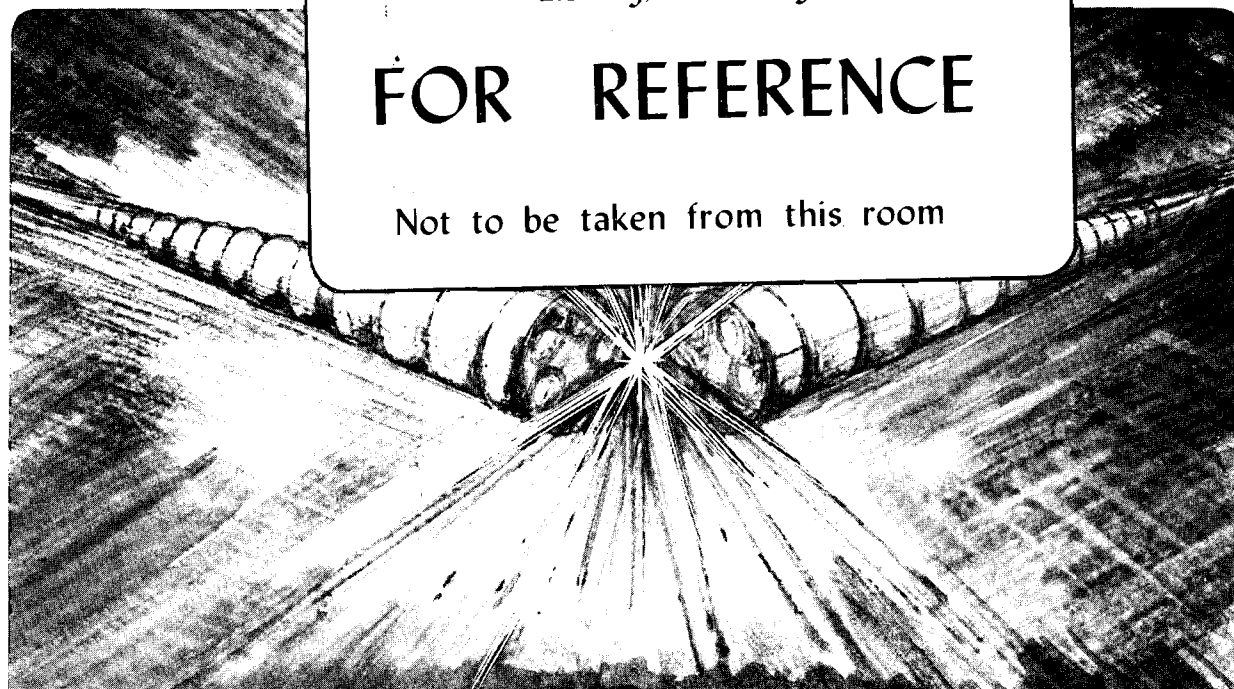
R.C.C. Perera

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**PHOTON EXCITATION FOR SATELLITE FREE X-RAY SPECTROSCOPY:
INSTRUMENTATION CHALLENGES***

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October 1991

Paper Presented at the 7th National Conference on Synchrotron Radiation Instrumentation,
Baton Rouge, Louisiana, October 28-31, 1991

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098

1. Introduction

In an attempt to produce radiation which would travel through matter opaque to ordinary visible light, Roentgen¹ in 1895 discovered x-rays. The potential of applications of x-rays in Science, Technology and Medicine were realized immediately.² Within a year, x-rays were widely applied in medical and industrial radiography. In 1910-1920, M. Siegbahn³ and co-workers developed the techniques for measuring wavelengths of x-ray absorption and emission spectra of the chemical elements. The effect of chemical combination on x-ray emission and absorption spectra was noted and well realized that the effect was small except for the lighter elements since valence electrons are more involved in chemical bonding than core electrons. Hence K and L x-ray emission and absorption spectra of light elements ($Z = 3$ to 18), that occur in the low energy x-ray region were investigated and soft x-ray spectroscopy was developed.

Lindh⁴, in summarizing earlier studies of S-K β emission spectra, showed that there is a great inconsistency between these measurements, mainly because measurements were obtained using direct electron bombardment, suggested using fluorescent x-ray excitation for x-ray emission spectral studies. The advantages of photon excitation over electron excitation were realized and the occurrence of satellites (or extra lines) in x-ray emission spectra was widely known. The extra features that appear in x-ray emission spectra in addition to the single vacancy (parent lines) transitions were known as satellites. Wentzel⁵ proposed the theory of satellites in x-ray spectra based upon a multivacancy processes, in which two or more electrons are excited or ionized, result in extra features. Later Langer⁶ and Wolfe⁷ studied the satellites in K α emission spectra to demonstrate the importance of the exchange interactions in determining the energy levels of the doubly ionized systems.

First systematic study of satellites in x-ray emission spectra was performed by Deslattes⁸ using quasi-monochromatic photon excitation from a group of L α x-ray sources lying close to the K edge of Cl. He observed significant alterations in the Cl K β spectrum of KCl depending on the character of the excitation radiation and identified the initial state of these satellites as a double vacancy state. Recently, the valence electronic structure of the chlorofluoromethanes were analyzed by chlorine K x-ray emission under satellite-free conditions.⁹ These studies were based on the use of synchrotron radiation to eliminate the multivacancy effects that are inherent in conventional x-ray spectroscopy.¹⁰ In this report, satellite free x-ray emission spectra from chlorofluoromethanes will be presented to demonstrate that the simplified spectra can be obtained using selective photon excitation. Results from various research groups world wide, utilizing the tunable photon excitation from synchrotron sources to eliminate the obscuring features in x-ray emission spectra of rare-gas solids (RGS) and metals will be discussed. Also, the technical challenges in utilizing the small phase-space attributes of high brightness from third generation SR sources producing soft x-ray and vacuum ultra-violet wavelengths to study weak features like satellites in x-ray emission spectra will be presented.

2. Results and Discussion

2.1 Molecular Gasses

Cl K absorption and Cl K-V emission spectra of several chlorofluoromethanes were measured using monochromatic radiation from X-24A beamline at National Synchrotron Light Source (NSLS) as the source of excitation. Detailed description of the soft x-ray beamline¹¹, monochromator¹² and experimental procedures⁹ are given elsewhere. As an example, results from CF₃Cl (gas phase) will be presented. In order to estimate contributions from satellite features in the x-ray emission spectra, Cl K-V fluorescence spectra were recorded at several incident x-ray energies in the vicinity of the single - and multiple - vacancy Cl K ionization threshold energies. Using the present Cl K-V emission data and UPS final state binding energies¹³, the Cl 1s ionization threshold of CF₃Cl is estimated to be 2830.2 eV. Hence, the 2833 eV photon excitation is an appropriate photon energy for producing satellite free spectrum, since the excitation energy is below all double vacancy threshold energies. The Cl K-V emission spectrum obtained using 2833 eV photon excitation is presented in Fig. 1 along with the Cl K-V emission spectrum obtained using 2880 eV photon excitation. The 2880 eV photon energy is above most [KV] double vacancy threshold energies, which correspond to production of initial states required for x-ray emission satellites in this energy range. As seen in Fig. 1, the 2880 eV spectrum (dots) contains extra contributions resulting from multi-vacancy transitions. The main satellite features thus obtained are located on the high energy side of the single-vacancy spectrum.

To facilitate interpretation of the experimental features in the present x-ray emission spectra, the spectra were modeled empirically¹⁰ using a SIMPLEX minimization technique. For the modeling, the instrumental broadening was assumed to be Gaussian and the natural line width to be Lorentzian, resulting in Voigt spectral profiles. The Gaussian instrumental broadening was estimated to be 1.0 eV by analyzing a series of x-ray emission spectra in this region. This value is consistent with direct measurements of the secondary-spectrometer resolution. The 2833 eV Cl K-V spectrum is presented again in Fig. 2 along with the modeled Voigt spectral components and their sum. Modeling of the x-ray emission spectra permitted extraction of energies and relative intensities of the emission peaks. Assignments were then determined by comparison with known valence molecular orbital (MO) orderings from UPS measurements.¹³

Because of selective excitation of CF₃Cl at 2833 eV, all emission features in the Cl K-V spectrum in Fig. 2 have a common initial state; namely, a single Cl 1s vacancy. Thus, the most probable transitions in the K-V emission spectrum involve electrons from valence MO's with Cl 3p character. The stronger emission components, peaks C and B, are assigned to dipole-allowed transitions of electrons in the 7e and 10a₁ valence MO's, respectively, filling the initial Cl 1s vacancy. The weaker emission peaks B' and A are assigned to allowed dipole transitions from the 5e and the 9a₁ + 4e valence MO's, respectively.

2.2 Rare-Gas Solids

RGS often used in the development of solid-state theory are bonded only by the weak Van der Waals forces in a FCC lattice. Therefore, uncomplicated satellite free x-ray emission spectra of RGS, which provide information about the partial density of states of the occupied valence bands will enable to test the rigorous band structure calculations¹⁴ performed on various solids. Perera and Henke¹⁵ measured the photon excited $L_{2,3}$ (3s-2p) emission spectra from gas and solid argon. Recently, high resolution soft x-ray emission measurements¹⁶ were performed by Jia *et al.*¹⁷ on solid Kr $M_{4,5}$ (4p-3d) and Xe $N_{4,5}$ (5p-4d) using monochromatic radiation from U-10A beamline at NSLS as the source of excitation. As an example of their work, the solid Kr $M_{4,5}$ (4p-3d) x-ray emission spectra excited with various photon energies are presented in Fig. 3. They observed that the previously reported¹⁸ satellite feature at about 82 eV is prominent when white light excitation is used and the satellite intensity decreases as the excitation energy is decreased. When a photon energy corresponding to a excitation energy below the multiple ionization threshold is used (103 eV photon excitation), the measured intensity in that energy region was extremely small. Furthermore, the previously observed¹⁸ satellite feature at 79.99 eV resulting from multiple ionization in krypton *via* Coster-Kronig decay of the L_1 hole state is energetically not possible. Therefore, the emission intensities observed in there 103 eV photon excited spectrum is a true measure of the p-like partial density of states of the valence band in solid Kr, a result that will stimulate the theoretical efforts on RGS. This is first time satellite free x-ray emission spectra from RGS were obtained using monochromatic synchrotron radiation to suppress the complicating satellites.

2.3 Metals

A series of experiments in x-ray emission spectra of metals were carried out by Nordgren¹⁹ and his co-workers²⁰ at the Hamburg synchrotron radiation laboratory (HASYLAB) at DESY, using radiation from the FLIPPER multipole wiggler beamline. The measured photon flux at the sample position of this beamline is about 10^{12} ph/s with energy resolutions between 0.5 eV and 10 eV in the 20 eV to 1 keV photon region. They measured²⁰ the Cu $L_{2,3}$ (3s-2p) spectra of copper metal excited using different photon energies as shown in Fig. 4. The 970 eV photon energy is sufficient to excite L_2 ($2p_{1/2}$) and L_3 ($2p_{3/2}$) hole states and the corresponding spectrum shows two bands resulting from the transitions from the 3s band to fill the $2p_{1/2}$ and $2p_{3/2}$ vacancies respectively. The 935 eV photon excitation is below the L_2 ($2p_{1/2}$) threshold energy but nearly above the L_3 ($2p_{3/2}$) threshold energy, therefore, should energetically remove the emission peak at about 950 eV corresponding to the transitions to the $2p_{1/2}$ hole state. The reduction in intensity of the emission peak at about 930 eV when 935 eV photon excitation is used, suggested the occurrence of satellite features²⁰ resulting from Coster-Kronig decay of the L_2 ($2p_{1/2}$) hole state, giving rise to L_3 ($2p_{3/2}$) multi-vacancy states. The difference spectrum shown in Fig. 4 clearly reflects the contributions from such satellite features yielding information about the shake-off probabilities.

The advantages of selective excitation for x-ray emission spectroscopy was also demonstrated¹⁹ when separate N K (392 eV) and Ti L₃ (394 eV) x-ray emission spectra of TiN was obtained²¹ even though they overlap in this energy range. They measured the N K emission spectrum of TiN using 410 eV monochromatized synchrotron radiation as the source of excitation (see Fig. 5). Since, the corresponding excitation energy is below the Ti L₃ threshold energy (453 eV), the spectrum presented in Fig. 5 is free of contributions from overlapping Ti L₃ x-ray emission. Furthermore, use of photon excitation closer to the N K threshold energy (409 eV) will eliminate the satellite features, resulting a true N K x-ray emission spectrum of TiN. This will enable the band spectrum mapping of the N 2p contributions to the valence band of TiN in an unambiguous way. Also shown in Fig. 5 is the Ti L₃ emission spectrum obtained using 458 eV photon excitation, an excitation energy lie between L₂ and L₃ threshold energies. The spectra presented in Fig. 5 are aligned to the Fermi energy by means of XPS binding energy data. They also measured²¹ Ti L emission spectra using photon energies well above and well below the L₂ threshold energy of 453 eV, and the difference spectrum presented in Fig. 5 thus represent the Ti L₂ (3s - 2p_{1/2}) emission spectrum of TiN. This is the first time undistorted N K, Ti L₂ and Ti L₃ emission spectra of TiN was measured, a measurement that will facilitate the band structure investigations of this compound. They also observed a new type of resonance in the Ti L emission spectra, resulting from the decay of a quasiautomatic intermediate state²¹.

3. Instrumentation Challenges

The technical requirements to study weak features like satellites in x-ray emission spectra are: high flux delivered to a small spot size, stable beamline optical system, tunability of the x-ray source (monochromatized) over a large energy range and a high resolution x-ray spectrometer to analyze the emitted photons. Third generation synchrotron radiation sources like Advanced Light Source (ALS) in Berkeley designed²² for dedicated experiments by photon users²³ is optimized for high spectral brightness in the soft x-ray and vacuum ultra-violet wavelengths. The undulator radiation from ALS can deliver high photon flux to a small spot size provided the design of the beamline do not diminish the spectral brightness through aberrations associated with the imaging properties or through the figure errors associated with the optical components. Because of the high photon fluxes and power loading, it is quite difficult to design a stable beamline optical system consisting of collecting mirrors, gratings, focussing elements, etc. that does not diminish the spectral brightness.

An insertion device beamline²⁴ at ALS is under construction utilizing radiation^{25,22} from a 5.0 cm period undulator (U5.0) to cover the 100-1500 eV photon range. Spectral flux in the central curve (0.1% band pass) as a function of photon energy for the U5.0 undulator is shown in Fig. 6. Each undulator curve is the locus of narrow peaks of radiation, tuned by altering the undulator gaps. Separate curves are shown in Fig. 6 for the first, third, and fifth harmonics of the undulator. A spherical grating monochromator (SGM), is similar to the one constructed²⁷ at ALS for another U5.0 undulator beamline with fixed grating rotational axis and fixed incoming and outgoing ray directions. Simple rotation of the grating provides the

energy tuning. The Rowland-Circle condition can be satisfied throughout the scanning range by moving the entrance/exit slits along the beam direction providing a good focus. The energy resolution of SGM is shown in Fig. 7 when the exit slit motion is about 0.7m. The monochromator utilizing three gratings, 200 l/mm, 500 l/mm and 1200 l/mm to cover the first, third, and fifth harmonics of the undulator respectively, results in a energy resolution $E/\Delta E$ better than 10^4 for the 100-200 eV region. The beamline output flux²⁶ at the exit slit for the U5.0 undulator beamline consist of a SGM and 10 μm entrance and exit slits are presented in Fig. 8. The flux transmission through the slits and grating efficiencies are included in these calculations. As seen from Fig. 8, using refocussing optics, over 10^{12} ph/s in a 0.1% bandwidth can be delivered to a 10 μm spot size.

One of the five end stations under construction to utilize this radiation is a high resolution soft x-ray emission (SXE) spectrometer²⁸, a grazing incidence, Rowland Circle instrument where the diameter of the Rowland Circle can vary from 5 to 10m. This spectrometer is designed to match the small phase-space attributes of high spectral brightness of the beamline optical system. Special features of the SXE spectrometer are four toroidal gratings on a carousel mount to cover the energy range of 40-1400 eV and a photon counting area detector in place of the output slit. The energy resolution ($E/\Delta E$) of the SXE spectrometer in this energy range is about 1000, sufficient to resolve features in x-ray emission spectra.

4. Conclusions

Tunable radiation from third generation synchrotron radiation sources like ALS when combined with a SXE spectrometer designed to match the emittance properties of these sources will enable to perform more difficult experiments discussed in this paper in a routine manner. Also, will able to extend these measurements to more difficult systems like gas phase studies, buried interfaces etc. and to obtain spectra with a higher resolution. It was noted¹⁵ several years ago that the satellite features in molecular gases and rare gases were less prominent in the solid phase. A comparison of satellite features in solid and gas phases will give a insight to the production of multi-vacancy states as well as the decay of the multi-vacancy hole states resulting from solid state effects. Also tunable radiation has the ability to "turn off" the multi-electron channels producing satellite features in x-ray emission spectra. Simplified spectra thus obtain can provide information about radiation yields, line widths and peak shapes in an unambiguous way and no other technique can attain this results.

The unique aspects of photon-in photon-out measurements are: threshold excitation provides spectral purity and sensitivity, photons are less damaging compared to other particles, provide bulk sensitivity and ultra high vacuum is not required. Photon-out phenomena can also be used in the presence of charged particles and strong electric and magnetic fields associated with the various deposition methods enabling to monitor on-line processing of thin films and layered structures.

5. Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. I wish to acknowledge valuable discussions with T.A. Callcott, P.L.Cowan, D.L. Ederer, P. Heimann, and J. Nordgren.

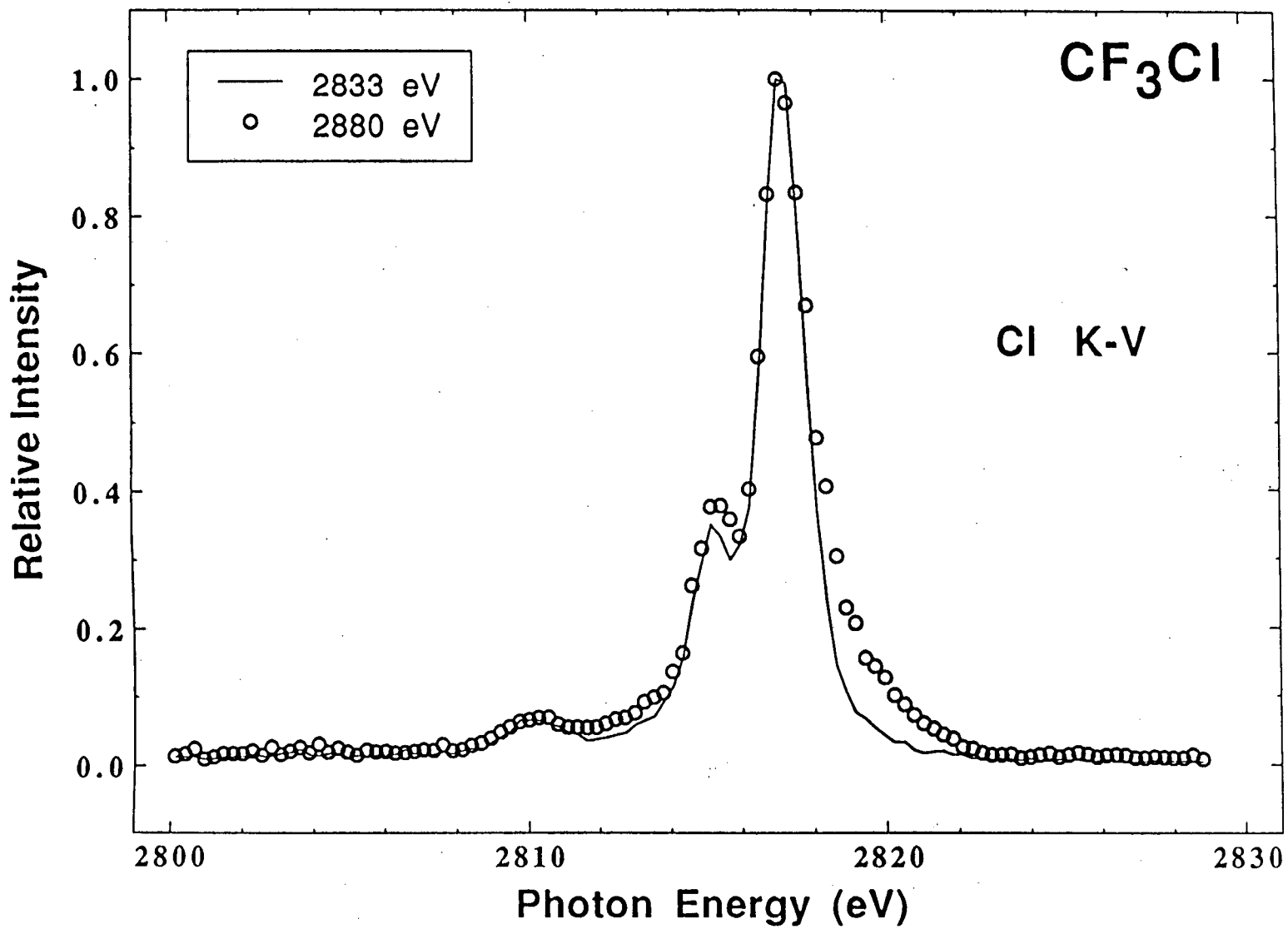
Figure Captions:

- Figure 1. Comparison of 2880 eV photon excited Cl K-V emission spectrum of CF_3Cl (circles) with a 2833 eV excited spectrum indicated by the solid curve. The increased intensity contributions in the 2880 eV excited spectrum are attributed to multi-vacancy transitions.
- Figure 2. Experimental 2833 eV photon excited Cl K-V emission spectrum of CF_3Cl (dots) along with the fitted spectral components (dashed curves) and the sum of the derived components (solid curves).
- Figure 3. The solid krypton $M_{4,5}$ (4p-3d) x-ray emission spectra obtained using monochromatized synchrotron radiation. The corresponding excitation energies are indicated above each spectrum. (J.J. Jia *et al.* Ref.17).
- Figure 4. The Cu $L_{2,3}$ (3s-2p) emission spectra of copper metal obtained using 935 and 970 eV photon excitations and the corresponding difference spectrum. (J Nordgren *et al.* Refs. 19 and 20).
- Figure 5. Nitrogen K and titanium L x-ray emission spectra of TiN. (J Nordgren *et al.* Refs. 19 and 20).
- Figure 6. Spectral flux in the central curve (0.1% band pass) as a function of the photon energy for the U5.0 undulator at ALS for the first, third, and fifth harmonics of the undulator. Each curve is the locus of narrow peaks of radiation, tuned by altering the undulator gaps. (P. Heimann Ref. 26)
- Figure 7. The energy resolution of the monochromator utilizing three gratings, 200 1/mm, 500 1/mm and 1200 1/mm to cover the first, third, and fifth harmonics of the undulator respectively. The exit slit motion is about 0.7m. (A.Warwick *et al.* Ref.27).
- Figure 8. The beamline output flux at the exit slit for the U5.0 undulator beamline consist of a SGM and 10 μm entrance and exit slits. The flux transmission through the slits and grating efficiencies are included in these calculations.

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Figure 1

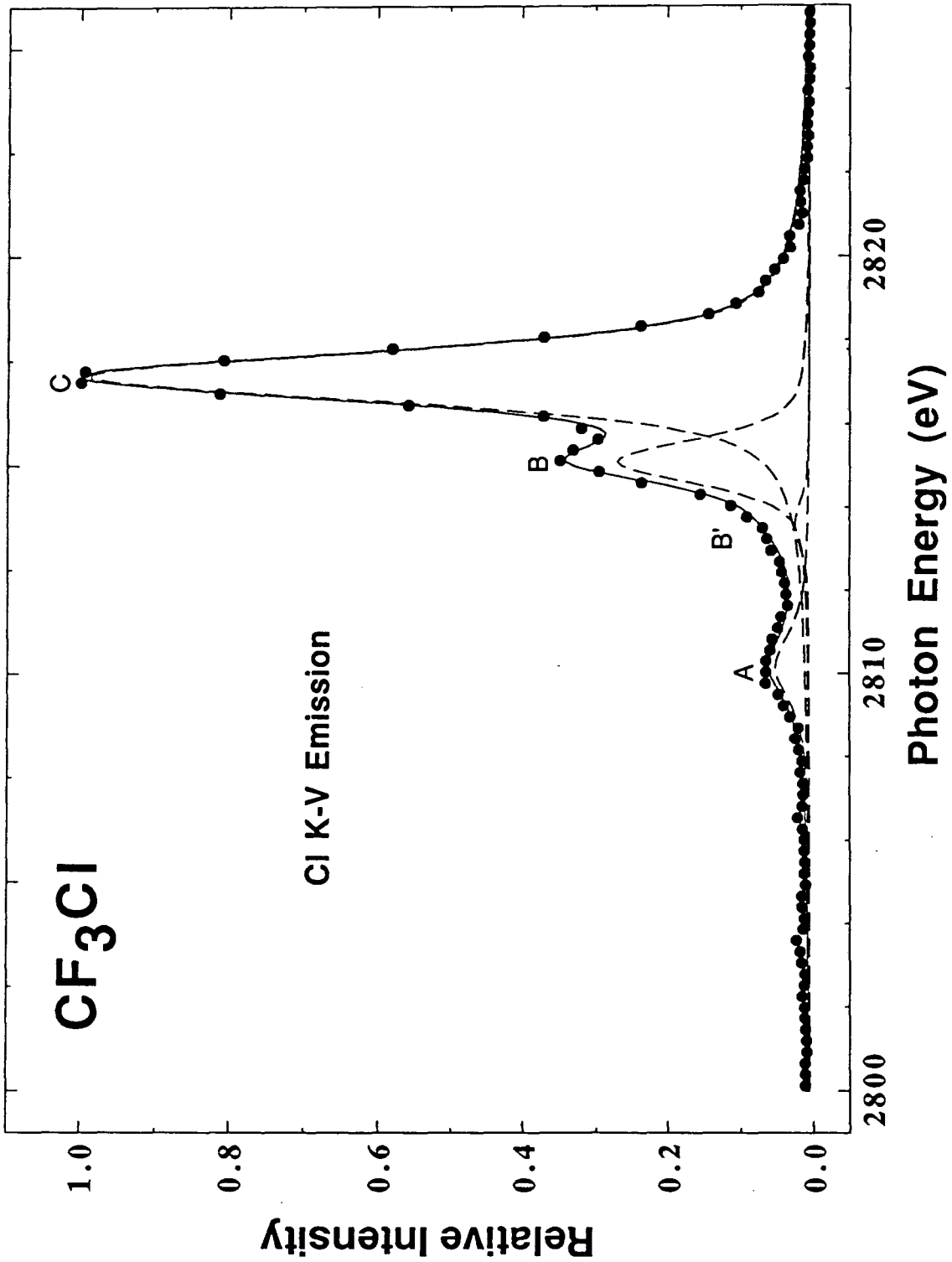


Figure 2

Solid krypton $M_{4,5}$ emission excited
by synchrotron radiation

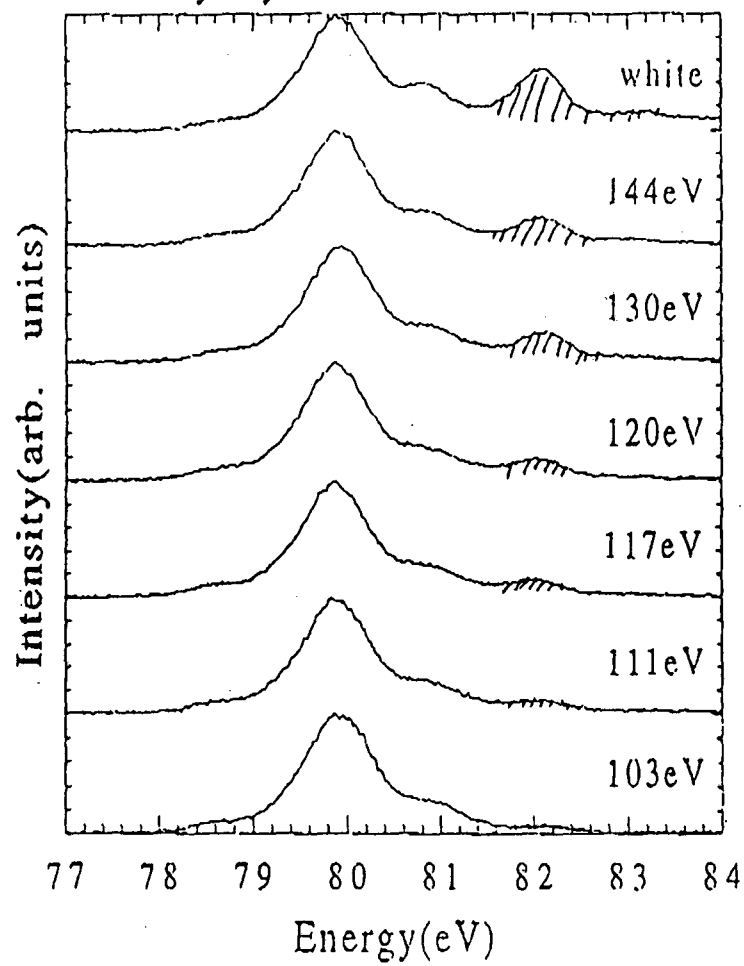


Figure 3

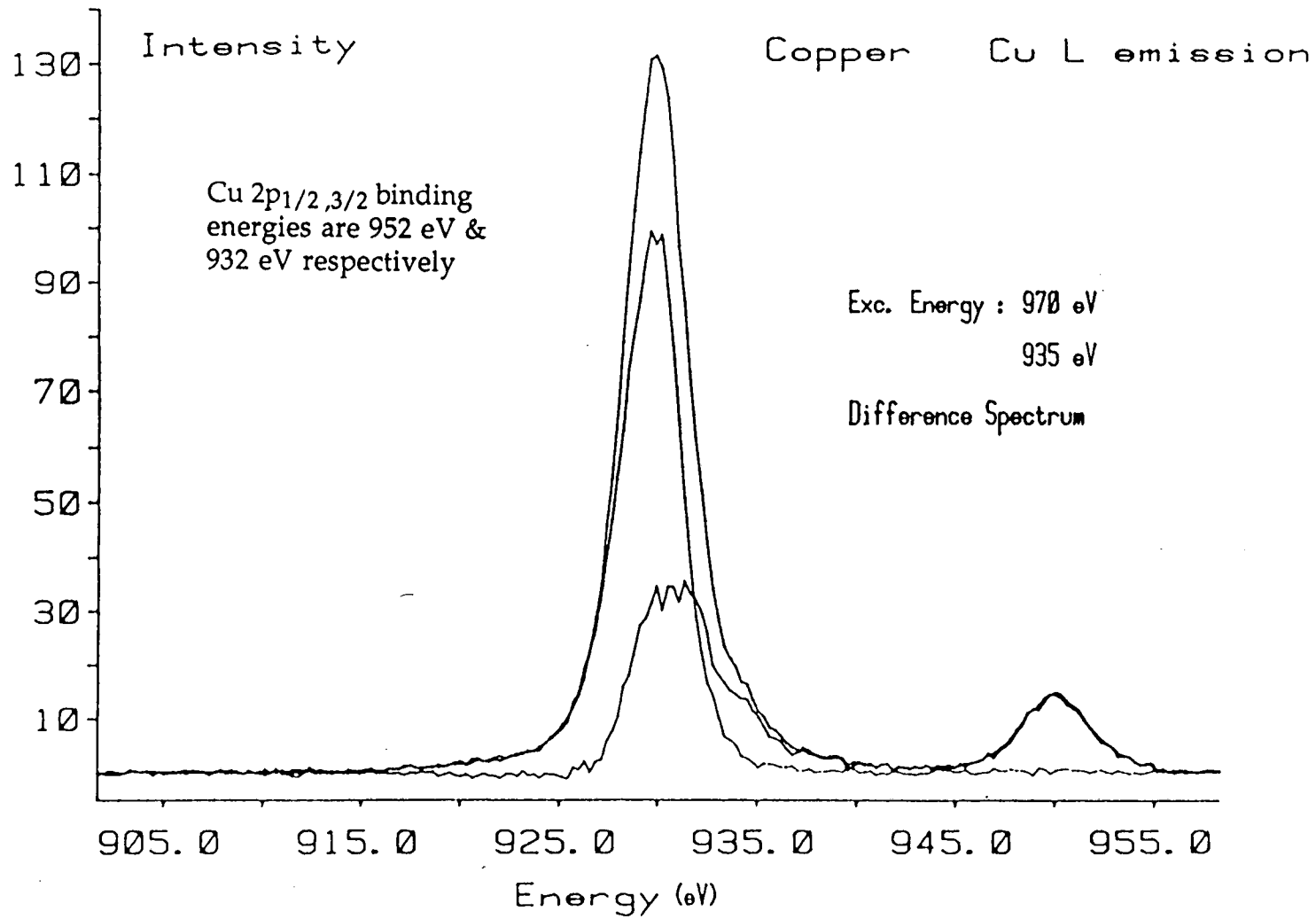


Figure 4

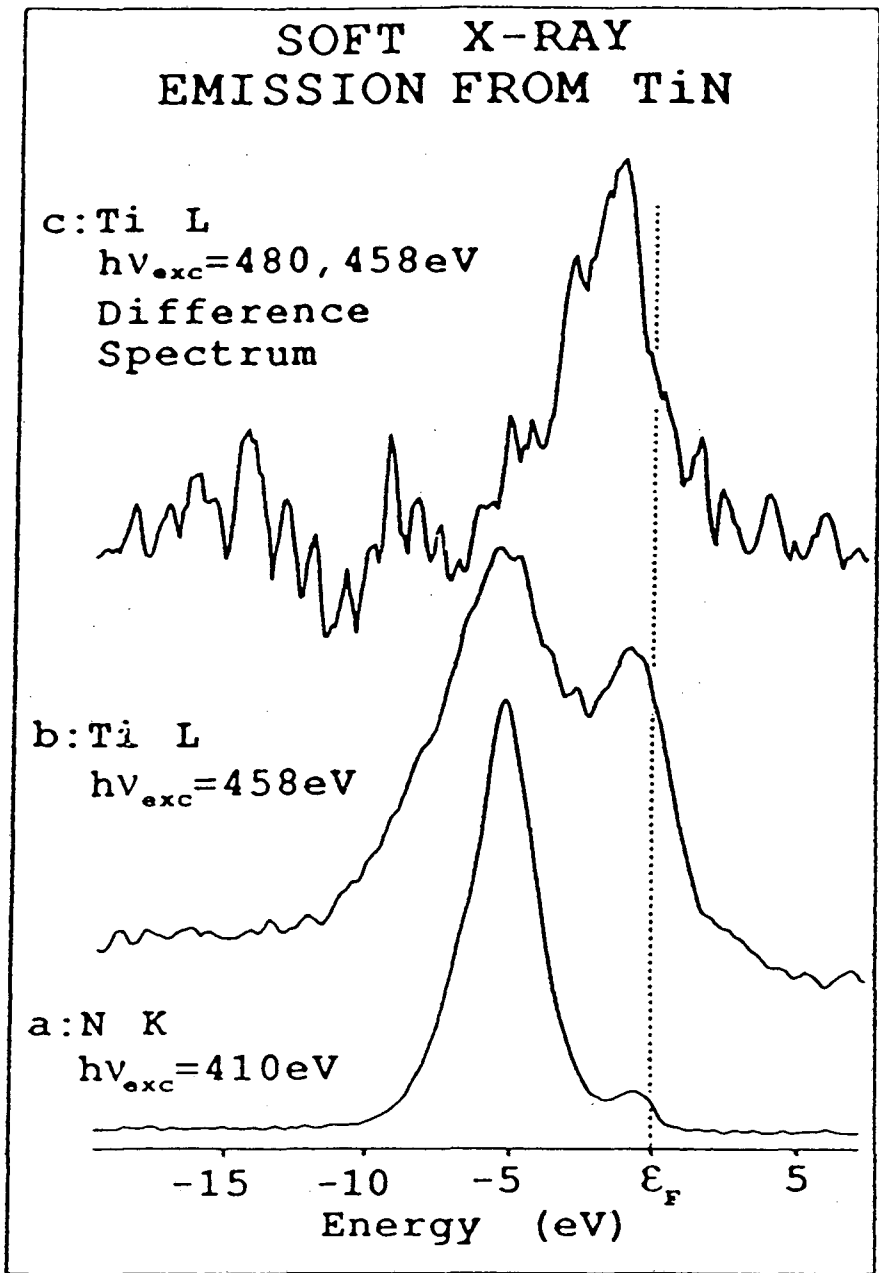


Figure 5

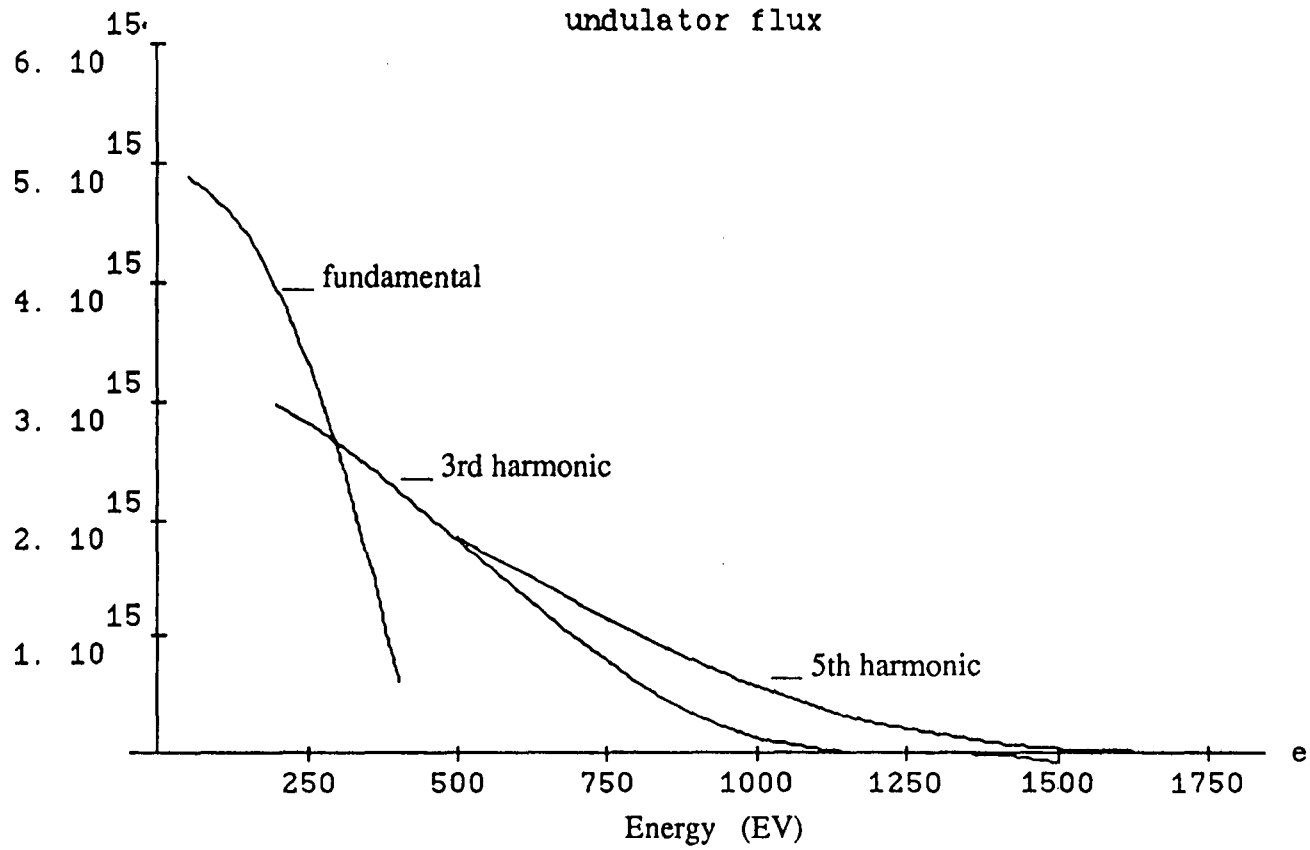


Figure 6

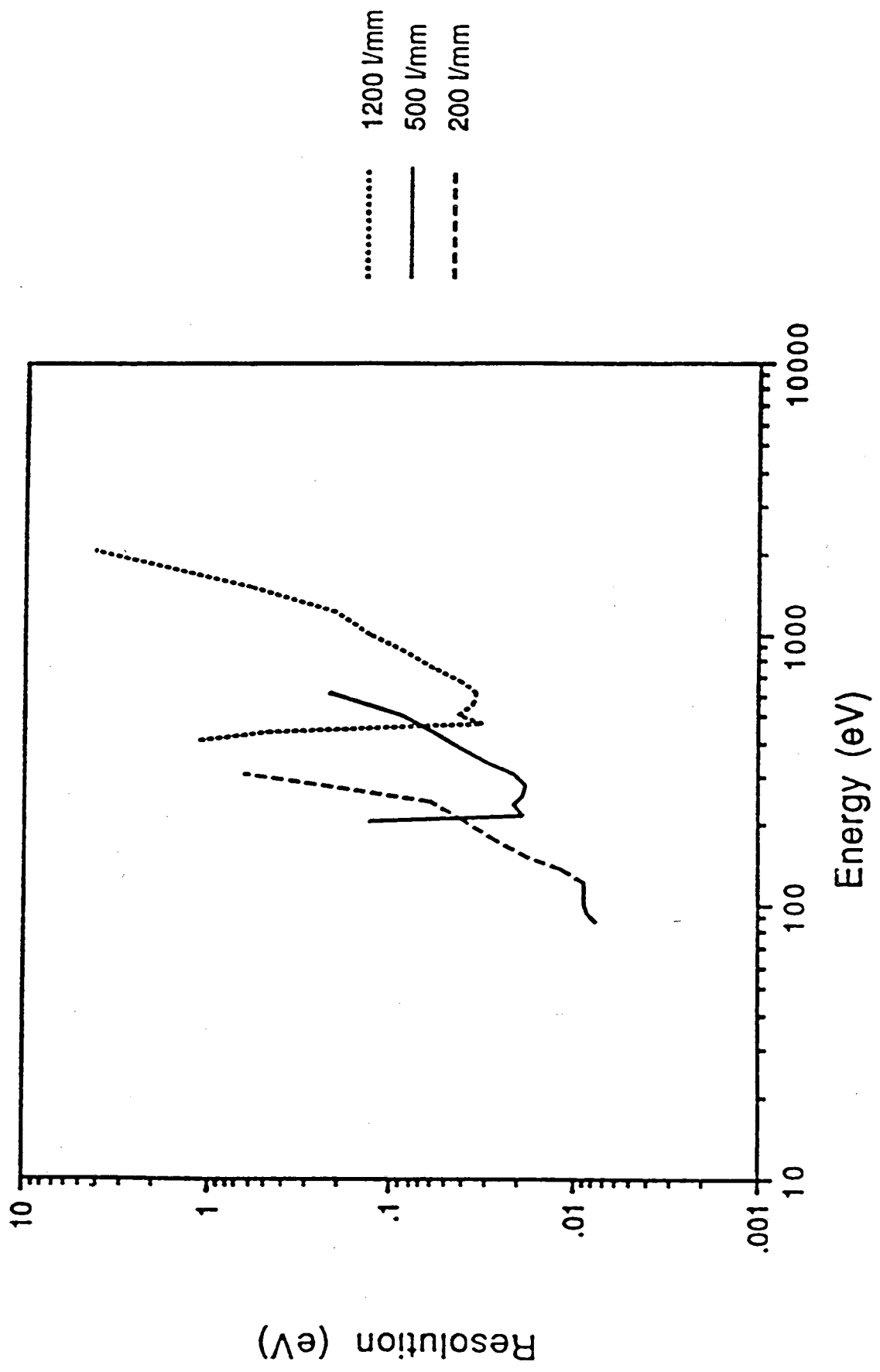


Figure 7

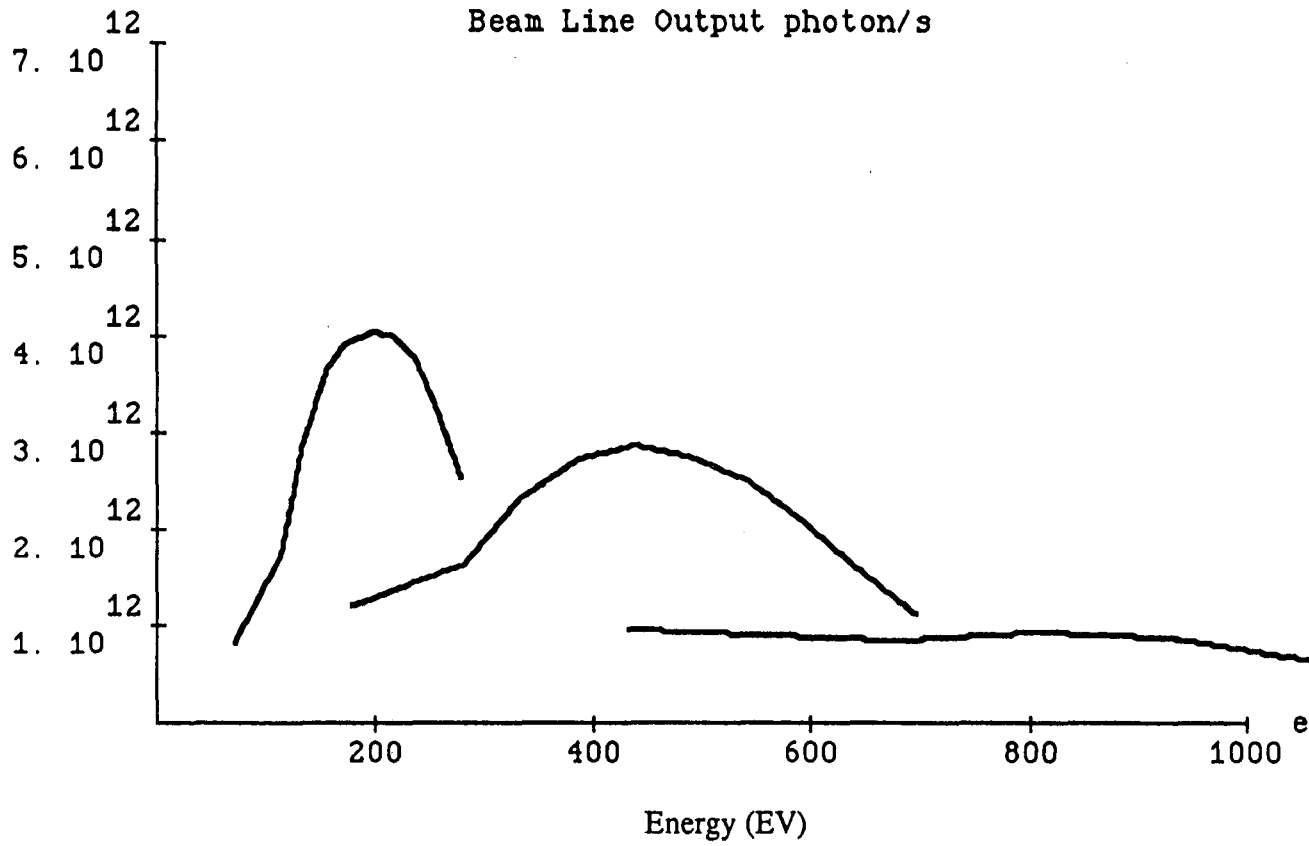


Figure 8

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