5. SCIENTIFIC ACTIVITIES

5.1 Atomic and Molecular Science

5-1-1 Introduction

Atomic and molecular science occupies a special place in research with synchrotron radiation. It is the area in which the very first experiments were performed. It is a very fundamental area investigating basic photoprocesses involving electron correlation in atoms as well as molecular potentials and dynamics transcending the Born-Oppenheimer approximation. To date, it has been the area which is perhaps the most demanding in terms of the light-source performance, requiring the highest resolution combined with high flux to overcome the tenuity of gas-phase targets and various highly differential detection schemes. Consequently, it has been a strong driving force for further developments and upgrades of synchrotron facilities and provides benchmarks for their performance. Another aspect is that the major part of the actual work tends to be in the development of experimental methods, devising various apparatus on-site, instead of involved sample preparation etc. that has to be done elsewhere. Therefore it is an area quite suitable for pursuit by the leadership of in-house staff members, together with close collaborators. Also, considering the local situation, the photon energy requirements in the VUV and soft-X region match very well with the characteristics of typical undulator sources at the Photon Factory 2.5 GeV ring.

Taizo Sasaki, former director of the Photon Factory, appreciated the importance of atomic and molecular science from the very beginning and emphasized it as a strategic area for the development of the Photon Factory, not only as an experimental facility but also as a research institute. Scarcity of strong established programs in other major laboratories in this area at the time was another incentive. Four beamlines were allocated from the outset and two brilliant young scientists, Kenji Ito and Akira Yagishita were hired to lead the enterprise.

Ito and collaborators pursued the relatively low photon energy region with ultra-high resolution, developing beamlines under the mentorship of T. Namioka. Major landmarks include collaborative research with K. Yoshino (Harvard Observatory) on rotationally cold molecules relevant to interstellar processes utilizing supersonic molecular beams and the ultra-high resolution 6VOPE. Threshold electron spectroscopy methods were developed in collaboration with R. Hall (LURE) and Y. Morioka (Univ. Tsukuba) mostly at the BL-20A NIM. Coincidence measurements in collaboration with Lablanquie et al. are now pursued at BL-16B. A new major project is the development of a magnetic-bottle type electron time-of-flight analyzer.

Yagishita, together with his associates (Eiji Shigemasa, later succeeded by Junichi Adachi) and collaborators, pursued activities in the somewhat higher EUV and SX region. The Ion Time-of Flight (ITOF) spectrometer was designed by Y. Sato (Tohoku U.) and then implemented with a metal vapor oven with the assistance of B. Sonntag visiting from Germany. The ITOF proved to be a reliable workhorse producing results elucidating the decay pathway following the photoexcitation of atoms, including metal vapours. Then he moved on to molecules, developing the symmetry resolved soft X-ray spectroscopy method with ion detection. It led to further studies on photoelectron angular distribution measurements from fixed-in-space molecules with electron-ion coincidence methods. More recently the velocity map imaging method was introduced. As another new direction, they have started exploring the area of photoionization of molecules in a strong laser field by synchrotron radiation. Most of the recent activities have taken place at BL-2C.

Yoshiro Azuma was hired later in the mid-nineties, took over the ITOF apparatus and utilized it for research on triply excited hollow lithium, as well as laser excited targets. This line of research has now advanced to the study of doubly and triply excited beryllium, in collaboration with S. Hasegawa (U. Tokyo) and T. Nagata (Meisei U.). New directions include work on atoms perturbed by external fields as well as time resolved studies of atomic processes via fluorescence and meta-stable atom detection, leading to the development of the Lifetime Resolved Fluorescence Spectroscopy (LRFS) technique. Most of the experiments are done at BL-16B and BL-3B, as well as at the Advanced Light Source, Berkeley.

Major independent users include the group of K. Ueda (Tohoku U.) who has now moved his operation away to SPring-8, as well as Y. Hatano (Tokyo Inst. of Tech.) who is now succeeded by N. Kouchi. Ueda worked on symmetry resolved spectroscopy of diatomic molecules, in a healthy competition with Yagishita's group. The Hatono/Kouchi group has been working on super-excited states of hydrogen and other diatomic molecules, with experimental methods including fluorescence detection. One also needs to mention the merged ion-beam photon-beam experiments performed by a collaboration led by T. Koizumi (Rikkyo Univ.) and Y. Itou (Josai Univ.) which championed the area of photoionization of positive ions, in the nineties.

The lack of man-power has always been a problem, particularly for in-house staff members, and efforts have been made to at least partially compensate for it. Yagishita has a joint appointment with the University of Tokyo Chemistry Department and directs graduate students. Ito has been continuing a fruitful collaboration with the French group of R. Hall, now succeeded by P. Lablanquie and F. Penan. Azuma has remained productive by working with a succession of foreign postdoctoral fellows over the last several years.

The next section lists the topics selected as "highlights" on recent Photon Factory Activity Reports (2000 – 2004), accompanied with a very brief summary and just one representative figure each. Recently, the number of external users has been on the decline, paricu-

larly after the departure of Ueda and his many collaborators to SPring-8. Nevertheless, research activities remain strong and the relative proportion of research output by in-house staff members appears to have increased. The importance of single bunch operation has increased with Azuma's radiative life-time related projects, Ito's magnetic bottle electron TOF project, as well as Yagishita's velocity map imaging experiments and laser coincidence experiments. The plan to implement "top-up" injection of the ring should be most beneficial for single-bunch operation which currently suffers from short life-time. New beamline construction and modification projects following the recent ring upgrade should consider seriously the needs of atomic and molecular science.

5-1-2 Recent Results Selected as Highlights on the PF Activity Report (2000 – 2004)

Dynamics of Two Auger Electron Emission in Xe 4d Photoionization

Coincidence spectra of a slow and a fast Auger electron in Xenon were obtained in the 4d threshold region where the post-collision-interaction (PCI) effects are expected to be enhanced [1]. After the photoionization event, two Auger electrons are emitted either simultaneously (double Auger: DA) or in sequence (cascade Augers: CA1, CA2): The distortion and shift of the peak due to pronounced PCI effects depending on the excess energy is shown on Fig. 1.

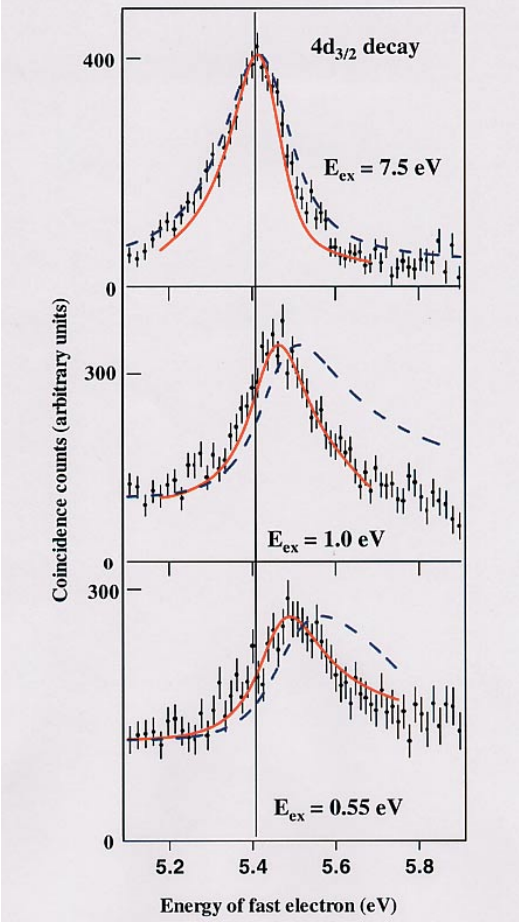

Figure 1
Coincidence Spectra of a slow and a fast Auger electron in Xenon. The 5.4 eV peak selects the decay of the $4d_{3/2}$ hole to the Xe^{3+} ground state. Calculations; full red line is CA2 process, broken blue line is DA or CA1 process.

Rotationally Resolved PFI-ZEKE Spectra of the $B^2\Sigma_u^+$ (v^+=0) State of N_2^+

The pulsed-field ionization zero-kinetic-energy photoelectron (PFI-ZEKE) technique, combined with the penetrating field threshold electron analyzer has made possible the rotationally resolved spectroscopic studies of molecular ions [2].

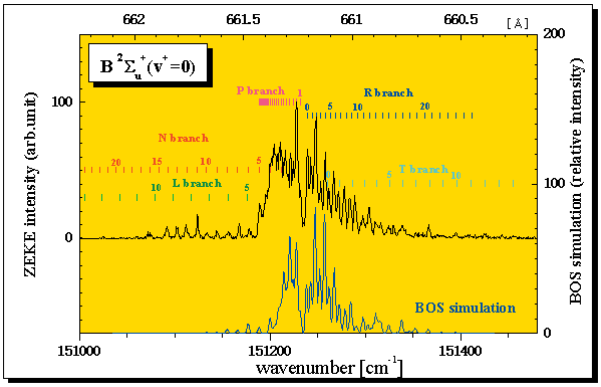

Figure 2
(Black line) PFI-ZEKE photoelectron spectra of nitrogen ($N_2^+B^2\Sigma_u^+(v+=0) \leftarrow N_2X^1\Sigma_g^+(v''=0)$) recorded with an extraction field of 0.8 V/cm between the dark gap of PF synchrotron. (Blue line) A simulation by the BOS model.

Effects of Light Polarizations on the $2\sigma_g$ Photoelectron Angular Distributions from Oriented N_2 Molecules

In addition to the photoelectron angular distribution for "fixed-in-space" molecules, this experiment also employed the variation of light-source polarization in order to approach the goal of a complete quantum mechanical experiment [3].

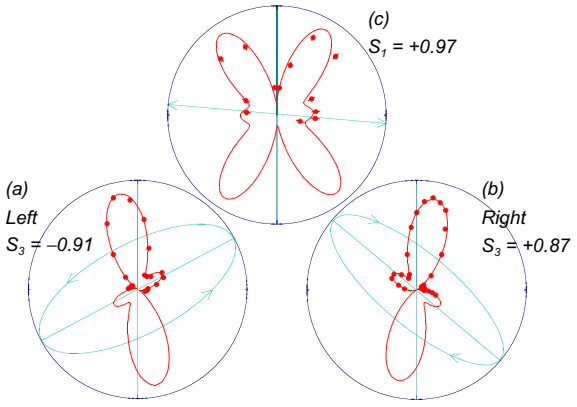

Figure 3
$2\sigma_g$ photoelectron angular distributions for N_2 molecules oriented along the vertical line: (a) left-elliptical polarization, S_1 = 0.42 and S_3 = -0.91 (b) right-elliptical polarization, S_1 = 0.50 and S_3 = 0.87, (c) linear polarization, S_1 = 0.97.

The Stark Quantum Beat of Ne Fluorescence in the Vacuum Ultra Violet Region

This experiment studied the effect of an external electric field on the atomic photoexcitation and radiative decay process. Interesting undulations were observed in the radiative decay curve obtained in measurements utilizing single-bunch operation. These are due to the interference between the coherently excited magnetic sublevels of the excited states, and the undulation period represents their splitting due to the external electric field [4].

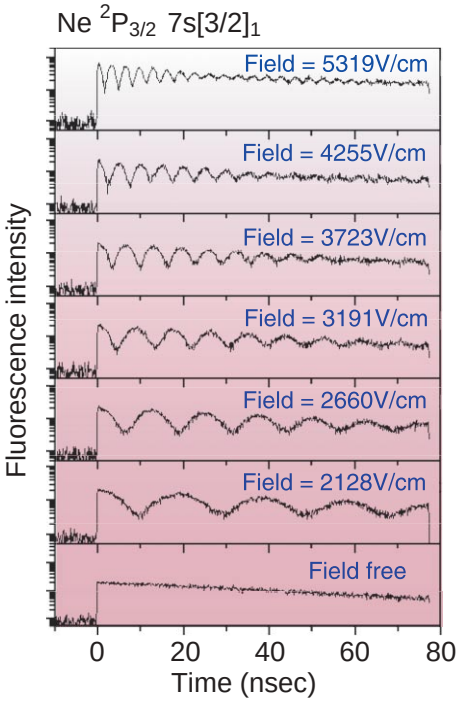

Figure 4
The fluorescence decay curve of the 7s[3/2]$_1$ states obtained with polarized radiation slanted at +45° to the *z* axis and at dirrerent electric field strengths.

Double Photo-Excitation of Helium in a Strong DC Electric Field

An atomic photoionization apparatus capable of applying more than 100 kV/cm over the interaction region was constructed. Photoion spectra of helium double photoexcitation resonances were obtained. In a strong electric field, significant distortion of the resonances as well as the appearance of new resonances was observed, seemingly defying the conservation of angular momentum [5].

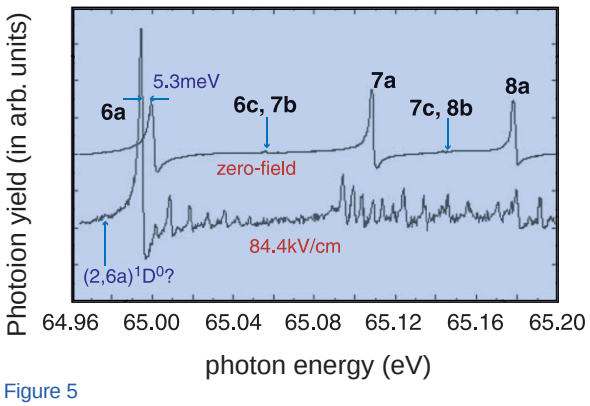

Figure 5
Photoionization spectra of helium double photoexcitaion resonances at zero-field and 84.4 kV/cm.

Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules:

The C 1*s* photoelectron angular distributions in the shape resonance region from fixed-in-space CO molecules with vibrationally-resolved resolution were measured for first time. The molecular-frame photoelectron angular distributions (MF-PAD) depends remarkably on the final vibrational state, due to the sensitivity of the potential barrier shape to the internuclear distance R [6].

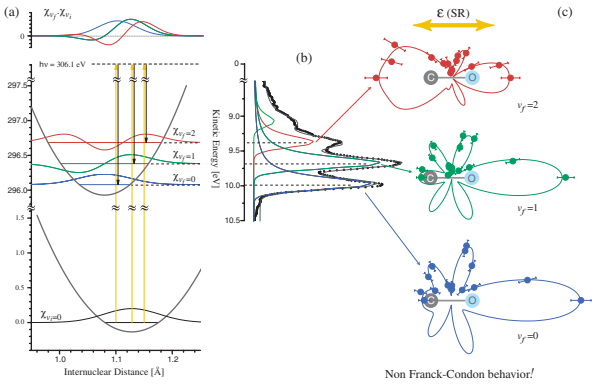

Figure 6
(a) Schematic potential curves of the CO molecule, the initial and final vibrational wavefunctions, and their product. (b) The vibrationally resolved C 1*s* photoelectron spectrum. (c) MF-PAD's for different vibrational final statess at *hv*=306.1 eV. The polarization vector of the incident light is parallel tothe CO molecular axis.

Large Resonances due to Doubly Excited States of Methane and Ammonia

The dynamics and spectroscopy of doubly excited molecules are interesting since the breakdown of both the independent electron model and the Born-Oppenheimer approximation are observed in them. We have

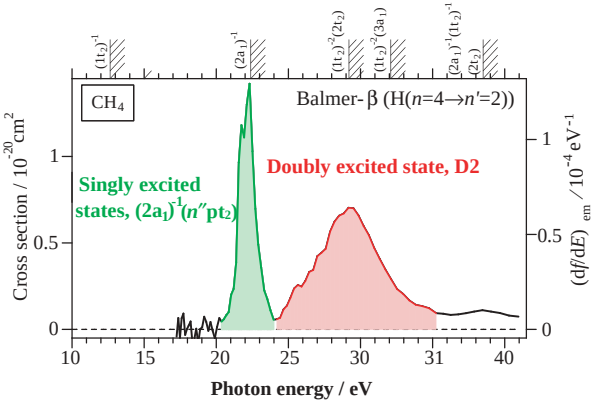

Figure 7
Cross sections (left axis) and oscillator strength distributions (right axis) for the H(n=4→n'=2) fluorescence in the photoexciation of CH_4 as a function of incident photon energy. The ionization potentials are also shown in the upper part.

measured the absolute cross sections for the emission of dispersed fluorescences from the excited hydrogen atoms in the photoexcitation of CH4 [7] and NH3 [8] as a function of incident photon energy in the vacuum ultraviolet range at BL-20A for the first time. The cross sections for the doubly excited states were found to be remarkably large.

Energy Exchange between Photoelectron and Auger Electron during Inner Shell Hole Decay

The post collision interaction (PCI) effects between photoelectrons and auger electrons were studied close to threshold where it is most enhanced. The combination of a threshold electron analyzer with a hemispherical analyzer was employed for coincidence measurements of threshold-photoelectrons and Auger electrons with argon 2p photoionization. This enabled the measurement of threshold electron yield showing PCI distortion associated with a particular auger decay channel [9].

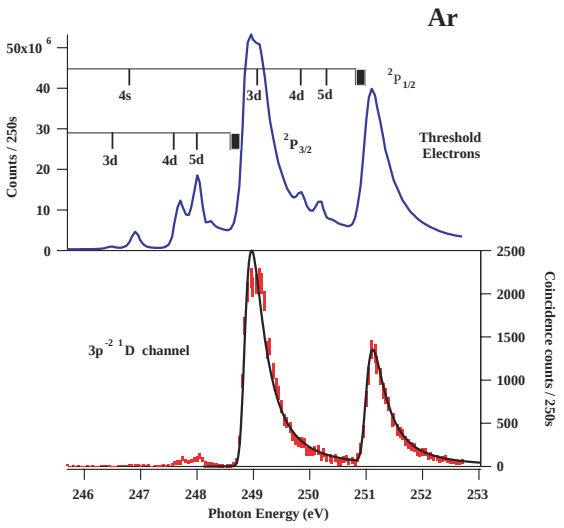

Figure 8
PCI process associated with ionisation of Argon in the 2p shell. Top: yield of threshold electrons. Bottom: yield of threshold electrons in coincidence with an Auger electron selecting the Ar^{2+} $3p^{-2}$ (^1D) final state (red bars) compared to theoretical predictions (black curve).

"Lifetime Resolved Fluorescence Spectroscopy" (LRFS) as a Sensitive Tool for Atomic and Molecular Excitation/Ionization Processes

Figure 9 shows a measurement of the He double photoexcitation resonances converging to the n=2 threshold. Single bunch operation of the ring was utilized. The photon energy was scanned and the time resolved spectrum of neutrals signal (vertical axis, coming from fluorescence and metastables) was measured at each photon energy step. It is to be noted that the tail of the peaks represents the radiative life-time of the doubly excited states. The sharp rise across the n=2 threshold is caused by photoion fluorescence. The photoion fluorescence profile in the vicinity of higher thresholds contain contributions from various decay channels having different lifetimes. These can be analyzed and spectra that are differential with respect to the final ionic state can be obtained (Lifetime Resolved Fluorescence Spectroscopy) [10].

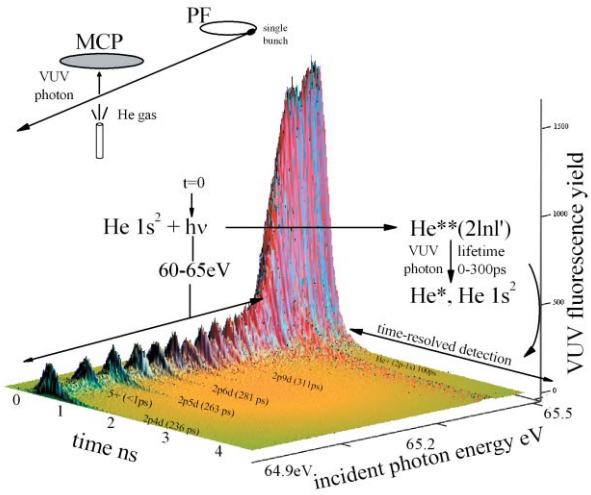

Figure 9
A two dimensional spectrum of neutrals (fluorescence and metastable atoms) signal detected by the MCP plotted against time (following synchrotron pulse) and incident photon energy. Peaks due to the fluorescence from double photoexcitation resonances of helium converging to the n=2 threshold are clearly seen. Metastables show as background parallel to the time axis.

References

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