

CONTRIBUTED POSTERS
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**ATOMIC
AND
MOLECULAR RESEARCH**

SPECTRAL PROPERTIES OF CONFINED ATOMS

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The energy spectra of ground-state, ionized and excited multielectron atoms and ions of the 3d and 4d periods of the Periodic Table centered in impenetrable spherical confinement are detailed using Hartree-Fock configuration average calculations. It is shown that, owing to modifications in 3d and 4d orbital collapse, the filling of shells for the transition sequence becomes more regular than for free atoms with increasing confinement pressure, that s-d competition ultimately disappears, and that, for d-excited states, the crossing between inner-shell excited states and the double-ionization threshold are altered. In general, the Periodic Table for confined atoms differs from that for free atoms.

The properties of hydrogen confined endohedrally at the geometrical center of a spherical, attractive short-range potential shell are explored. The evolution of the energy spectrum, as a function of the depth of the shell, is found to exhibit avoided crossings and unusual degeneracies. In addition, a new level ordering, principally by the number of nodes in the radial wavefunction, develops. The results apply generally to endohedrally confined atoms.

With the use of the above model, the origin and nature of confinement resonances in photoionization spectra of endohedrally confined atoms is established. Also found is that near-threshold resonances demonstrate significant sensitivity to the size and thickness of the shell and develop modulations in their intensities as a function of the confinement parameters.

A novel effect - the effect of selective orbital compression in endohedrally confined atoms is demonstrated. It turns out that even an attractive shell can exert positive pressure on an atomic orbital, making its size even smaller than the radius of the confinement itself.

It is shown that confinement can produce a significant redistribution of oscillator strengths in endohedral multielectron atoms, making the dominant transitions no longer superior but inferior in strength, and also making electron correlations in such atoms act in the opposite way to free atoms. This is exemplified by calculated results for endohedral Ca.

It is found that non-dipole effects in low energy photoionization of atoms surrounded by a repulsive semi-transparent potential can be increased by many orders of magnitude due to virtual levels occurring in the spectra of photoelectrons as a result of confinement. The strengths and widths of such resonances in non-dipole channels can be controlled by altering the characteristics of the confining potential, and under certain circumstances can be so large that treating quadrupole transitions as a perturbation breaks down, even for photon energies as low as tens of eV.

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CORE-CORE AND CORE-AUGER ELECTRON CORRELATIONS IN DOUBLE AUGER PROCESSES IN NE

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Using the photoelectron-photoion coincidence technique with energy dispersed electrons we measured the yields of the photoions upon the decay of the $Ne1s^{-1}$ state [1]. The yield of the Ne^{3+} ions which is roughly the probability of double Auger processes (DAP) was found to be $5.97 \pm 0.16\%$. Our configuration-interaction calculation of only the correlations of core electrons (core-core) gave the total DAP probability of 3%. Earlier many body perturbation theory calculation [2] gave 4%.

In ref. [3] the contribution to DAP in Ne due to the correlations of core and Auger electrons (core-Auger), *i.e.* inelastic scattering of the Auger electron by core electrons, is calculated with inclusion of only radial correlations, *i.e.* those where core and Auger electrons are excited into the states with the same orbital quantum numbers. The calculation [3] gave about 2% probability of DAP for each final state of the KLL transitions.

In this work we calculate the contribution to DAP from correlations of core and Auger electrons with inclusion of both radial and angular correlations (the excitations to all possible channels with l up to 3 are considered). Calculated DAP probabilities are presented in Table 1. Total calculated DAP probability is close to the experiment. Therefore, core-core and core-Auger electron correlations are the principal mechanisms of double Auger processes in Ne

Table 1. Probabilities (in %) of double Auger processes in Ne

Final state	Type of correlation	
	core-core [1]	core-Auger
$1s^2 2s^0 2p^6 \epsilon s$	8.16	3.94
$1s^2 2s^1 2p^5 \epsilon p$	4.87	2.45
$1s^2 2s^2 2p^4 \epsilon \{s,d\}$	1.12	2.05
Weighted total probability of the K-LLL DAP	5.37	

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A VAPOUR PHASE STUDY OF PHOTOIONISATION OF TIN

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The photoelectron study of electronic structure of metals as free atoms has been actively studied since the introduction of synchrotron radiation. Recently, the research in this field has become more active as the light sources and also experiments have developed allowing more accurate studies.

We have studied the photoionisation of the 5p, 5s and 4d orbitals in vapour phase atomic Sn, which have not been reported earlier, as far as we know. The measurements were carried out using synchrotron light at the beamline I411 of the third generation light source MAX II in Lund, Sweden. The vapour was generated using home-made resistively heated oven and the photoelectrons were detected with a high resolution Scienta SES-100 electron spectrometer. Figure 1 presents a Sn 4d photoelectron spectrum measured with photon energy of 60.6 eV.

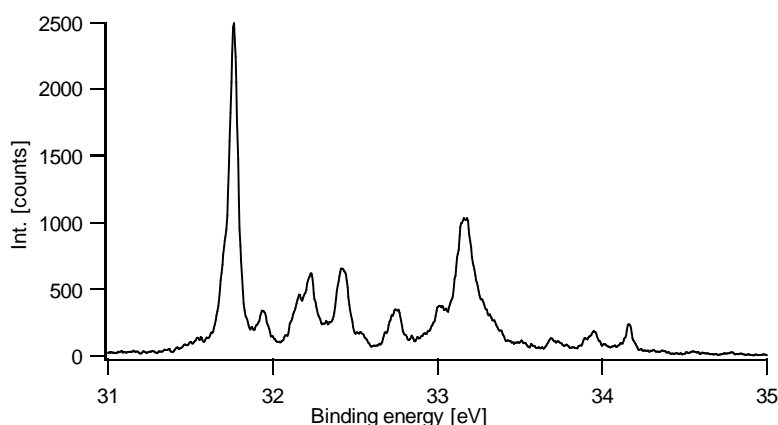


Figure 1: Photoelectron spectrum of Sn 4d orbital ($E_{\text{photon}} = 60.6$ eV)

Sn is an open shell atom with the electronic configuration of $[\text{Kr}]4d^{10}5s^25p^2$. Consequently, several close-lying neutral states are populated at the high temperature ($T \approx 1400\text{K}$) of our experiment, giving rise to multiple sets of peaks in the photoelectron spectra. The intensity distribution in photoelectron spectra of Sn has been predicted by relativistic Dirac Fock calculations applied to the thermally distributed initial states. The results have been found to be in good agreement with the experimental data.

ELECTRONIC AND ENERGY TRANSFER IN H₂O@Rg CLUSTERS (Rg=He, Ne, Ar)

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We have studied the electron and energy transfer in large Rg_N-clusters doped with H₂O molecule under photoexcitation in the 9-30 eV range (140-40 nm). The mean cluster size is varied from N=400 (argon) to 5·10³ (neon) and ≥10⁴ (helium). The reaction channel has been characterized by fluorescence of neutral OH* and H* and ionic H₂O^{+*} fragments. The measurements have been performed at the CLULU experimental station at HASYLAB. Rg-clusters have been prepared in a continuous free-jet expansion of a pure rare gas through an orifice-type nozzle of 40 μm diameter or through a conical-shaped nozzle (D=200 μm, 2θ = 4°). The nozzle is mounted on a liquid He cryostat and it can be cooled down until temperatures below 10K. Rg_N@H₂O-clusters have been prepared by a crossbeam technique. Tunable SR (Δλ=0.05 nm) is focused on the doped cluster. UV-visible fluorescence spectra are collected with a liquid nitrogen cooled CCD camera installed after a monochromator (f=275 mm, 150 or 1500 l/mm gratings). The background pressure is kept below 10⁻³ mbar during experiments by continuous pumping of the interaction volume.

As it is well known, a free water molecule predissociates under the VUV excitation above 9.137 eV yielding the OH(A-X) fragment emission. At higher excitation energy the fluorescence bands belonging to neutrals OH*, H* and ionized H₂O^{+*} excited products appear. We have observed an efficient energy transfer from Rg-matrix to the doped H₂O molecule. A strong difference in the reaction yield has been observed when going from free water molecule to that one embedded in different rare-gas clusters. The predissociation channel is found to be unaffected by the helium cluster environment. On the other hand, the ionization exit channel (H₂O^{+*}) seems to be suppressed inside both helium and neon clusters in favor of the fragmentation into neutral excited products. Additionally, the neon cluster strongly affects the neutral reaction channel. At 17.7 eV excitation instead of strong Balmer series H*(β,γ,δ,ε), which is characteristic of a free water molecule and of H₂O@He_N clusters, only the intense OH(A-X) emission has been observed. The same result has been observed in experiments with H₂O@Ar_N clusters. It has been found that higher energy excitation induces higher vibrational excitation of the OH*(A) fragment; the rotational temperature in the same time is lower. Our calculations show that OH*(A) is rotationally thermalized inside Ne-clusters with the temperature as low as 10K. A bimodal J-distribution of the OH*(A) fragment has been found in Ar-clusters. This effect is attributed to a different geometric position of the H₂O molecule in/on the Rg-cluster. This difference is apparently related to the Rg-Rg and Rg-H₂O pair potentials. In contrast to the case of He or Ne clusters, water molecule does not entry the Ar-cluster and takes the surface site.

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CAGE EFFECT IN PHOTODISSOCIATION OF H₂O MOLECULE IN Ar-CLUSTERS

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We study a caging of an electronically excited fragment OH^{*}(A) after VUV excitation of rare-gas clusters (Rg=He,Ne,Ar) doped with H₂O molecule. The measurements have been performed at the CLULU experimental station at HASYLAB. Our results indicate that by using the standard crossbeam technique we are unable to achieve the bulk site doping of the Ar-cluster by a water molecule. This is apparently related to the difference in Ar-Ar and Ar-H₂O interaction potentials. In order to overcome this limitation we have employed a three-crossbeam technique. The conical nozzle (D=200 μm, 2θ = 4°) was a source of large host clusters made of light atoms (Ne in our case). The first crossbeam dopes the Ne_N-clusters (N~5000) with water molecules, which take the sites in the interior of the cluster; the second crossbeam dopes the H₂O@Ne_N cluster by Ar-atoms.

Since the temperature of Ne-clusters is very low (~10K, the temperature of Ar-clusters is ~35K), Ar-atoms freeze around H₂O molecule inside the Ne-cluster and the low temperature prohibits the structural rearrangement in the embedded H₂O@Ar_m cluster. Because of its small size and a low concentration of the doped H₂O@Ar_m@Ne_N clusters, we used to excite them in the first excitonic band of the large host Ne-cluster at ~70 nm. Additional experiments performed with the Ar@Ne_N and H₂O@Ar_N clusters show that an efficient energy transfer exists between the excited host cluster matrix and the doped center in each case. These experiments give evidence that after Ne-cluster matrix excitation the energy can be efficiently transferred onto the water molecule surrounded by Ar-atoms in the composed multishell cluster.

We have measured the OH(A-X) fluorescence spectra as a function of the Ar-crossbeam intensity, which has been done by a variation of the stagnation pressure (P_{Ar}). The size of the Ar-cluster formed around a water molecule is proportional to P_{Ar}. We have observed a strong decrease of the OH^{*}(A) emission intensity at the argon crossbeam pressure above 20 mbar. A second decrease of the intensity seems to exist at the pressure higher than 70 mbar. Except for these points the fluorescence band intensity exhibits only a small variation. We attribute this feature to the cage effect of Ar-atoms on the H₂O photodissociation fragments: being caged, OH^{*} and H have high probability to be quenched through the H₂O(X) potential. We believe that at the crossbeam pressure of 20 mbar the first shell of Ar-atoms (m₁=12) is almost formed around the water molecule. The subsequent decrease of the emission intensity above 70 mbar may indicate the formation of the second atomic shell (m₂=54) of the Ar_m cluster. These studies can be helpful in understanding of the solid structure formation in small rare gas clusters.

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Measurements of double photoionization ($\gamma, 2e$) in atomic Sr

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We present measurements of the differential cross section for double photoionization (DPI) of Sr vapour, collected at the Daresbury Synchrotron Radiation Source. Electrons from the $5s^2$ shell are analyzed in energies by electrostatic hemispherical analyzers and detected in coincidence; the radiation energy is tuned at an energy resonant with the $4p \rightarrow 4d$ excitation (25.25 eV).

Measurements are reported for equal (4.26 eV) and unequal (6.76 and 1.76 eV) energies of the two electrons; both electrons are observed in the plane perpendicular to the photon beam. One electron is detected either parallel ($\theta_1=0$) or perpendicular ($\theta_1=90$) to the \mathbf{E} field of the partly linearly polarized radiation.

In figure 1 the coincidence pattern for equal electron energy is displayed as a function of the relative angle of emission. It is clear that the present data show evidence for antiparallel emission of the two electrons. This is against the selection rules imposed by the dipole approximation and 1S_0 symmetries of the initial and doubly charged final states, that predict a node for antiparallel emission of the two electrons. We tentatively explain this anomalous result either by the presence of two unresolved maxima close to and either side of $\theta_{12}=180^\circ$, or by a 3P component in the $4p \rightarrow 4d$ resonance.

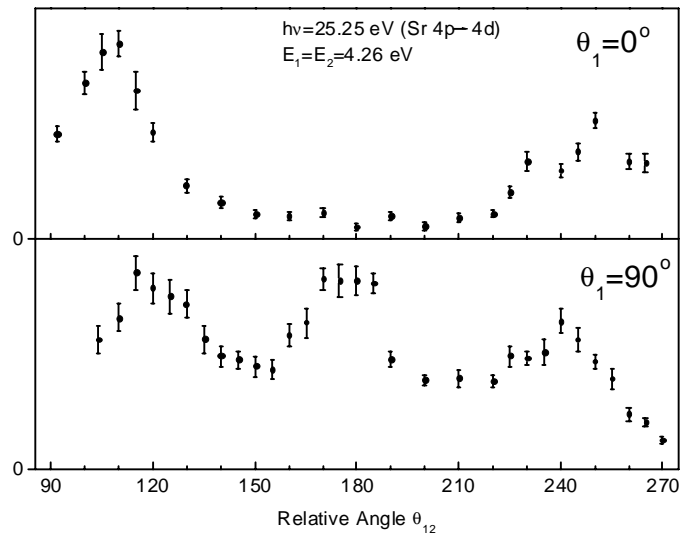


Figure 1: Coincidence pattern of electrons emitted with the same kinetic energy in the plane perpendicular to the photon beam. One electron is emitted either parallel ($\theta_1=0$) or perpendicular ($\theta_1=90$) to the polarization of the radiation.

PHOTON YIELD FROM SOLID KRYPTON AND XENON AT THE EDGE OF EXCITON ABSORPTION

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Spatial and temporal fluctuation of the lattice potential caused by phonons and deformability of the lattice induce the broadening and existence of low-energy tail of the excitonic absorption spectra and dressing of excitons by phonons, which leads to self-trapping of excitons [1]. Relaxation of electronic excitation in rare gas solids results in formation of variety of trapped centers [2]. Recently the effect of molecular trapped centers associated with lattice imperfections on the shape of excitation spectra of excitons has been reported [3]. In the present study the time-resolved fluorescence excitation spectroscopy in the VUV has been used to study the effects of crystal lattice perturbations on relaxation of excitons in solid Kr and Xe. The experiments were performed at the SUPERLUMI experimental station at HASYLAB, DESY, Hamburg. The excitation spectra of solid Xe and Kr were measured in the energy range of $n=1$ exciton absorption. Figure 1 shows the decay curve of free-exciton luminescence and selected excitation spectra of solid Xe, which were measured in three time windows Δt with delay δt relative to excitation synchrotron pulse: 1) window W1 ($\Delta t=1.5$ ns, $\delta t=0$ ns); 2) window W2 ($\Delta t=2$ ns, $\delta t=1$ ns); and 3) window W3 ($\Delta t=32$ ns, $\delta t=5$ ns). The effects of interaction of free excitons with neutral and charged intrinsic trapped centers are discussed.

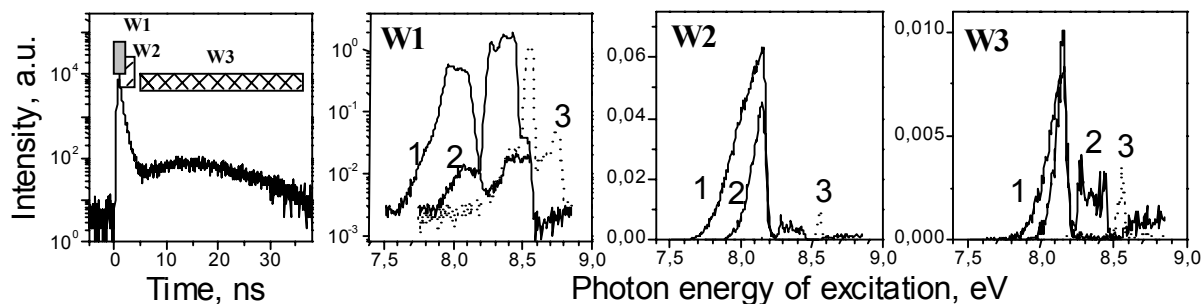


Figure 1: Decay curve of free-exciton luminescence (excitation with $h\nu=8.86$ eV) and excitation spectra measured at photon energies (1) 8.05 eV, (2) 8.36 eV, (3) 8.67 eV within time windows W1, W2, W3 indicated above the decay curve by rectangles.

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First observation of resonant Auger decay of Xe $3d^1 6p$ to Xe⁺ $4d^2 nl$

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The resonant Auger (RA) process, where a system with an inner-shell electron promoted to an unoccupied orbital decays by electron emission, has received considerable attention during the last decade [1]. Recent improvements on optical resolution of soft X-ray monochromators installed in the undulator beamlines of synchrotron radiation facilities made it possible to observe RA emission spectra (RAES) with overall widths narrower than the core-hole lifetime widths.

We have recorded, for the first time, angle-resolved RAES arising from the transitions Xe $3d_{3/2}^{-1} 6p_{3/2} \rightarrow \text{Xe}^+ 4d^2 6p_{3/2}$ and $4d^2 7p_{3/2}$ in the kinetic energy region of 520-530 eV. The experiments were carried out on beamline 27SU at SPring-8 using an ultrahigh-resolution hemispherical electron spectrometer (Gammadata-Scienta SES2002). The overall widths were less than 100 meV, far narrower than the core-hole lifetime width of 500 meV. At this resolution the splitting due to the coupling between the Rydberg electron ($6p_{3/2}$ or $7p_{3/2}$) and the doubly-charged ionic core ($4d^2$) were partly resolved.

The energies of RAES are ~ 4.7 eV lower than those of the corresponding normal Auger emission spectra. With the help of the spectator model [2], where the wave function of the excited electron is assumed not to change during the de-excitation process, the asymmetry parameters β and branching ratios for each transition in RAES can be related to those for the corresponding normal Auger transitions. The corresponding $M_5 N_{4,5} N_{4,5}$ normal Auger transitions have been studied both experimentally [3] and theoretically [4]. Comparing the asymmetry parameters β and branching ratios measured for the RA lines with those predicted from the normal Auger data, we could assign most of the observed RA lines.

This experiment was carried out with the approval of the SPring-8 program advisory committee and supported in part by Grants-in-Aids for Scientific Research from the Japan Society for the Promotion of Science and by the Matsuo Foundation. We are grateful to the staff of SPring-8 for their help.

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HIGH-RESOLUTION C 1s and F 1s RESONANT AUGER EMISSION IN THE TETRAFLUOROMETHAN MOLECULE

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We recorded angle-resolved resonant photoemission spectra of CF₄ in the excitation regions of C 1s and F 1s to the lowest antibonding molecular orbitals σ^* . The measurements have been carried out on beamline 27SU at SPring-8, using a high-resolution electron energy analyser (Gammadata SCIENTA SES2002). In figure 1, the valence photoemission spectrum of CF₄ recorded at the photon energy resonant with the C 1s $\rightarrow \sigma^*$ excitation is compared with the non-resonant spectrum; both collected in the direction parallel to the polarisation vector. The overall energy resolution was <50 meV. The tail of the C ²T₂ band towards high binding energy in the resonant spectrum is evidence of enhanced nuclear motions in the core-excited states; no such enhancements are observed for the D ²A₁ bands. Vibrational structure is not resolved in the high binding energy part of the C ²T₂ band, due to overlap of non-totally symmetric vibrational modes with the totally symmetric breathing mode; the non-totally symmetric vibrations are highly excited through vibronic couplings in the core-excited states. This effect is present also for F 1s excitation but is less dramatic, reflecting that the nuclear motion is less significant in the F 1s ¹ σ^* state, due to shorter lifetime, than in the C 1s ¹ σ^* state.

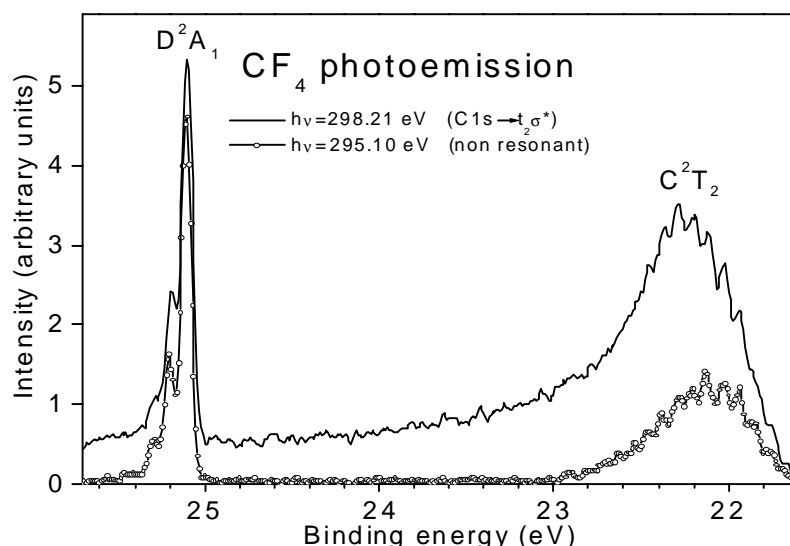


Figure 1: Photoemission spectrum of CF₄ recorded at photon energy resonant with the C 1s $\rightarrow t_2 \sigma^*$ excitation, compared with a non-resonant spectrum.

NEAR-THRESHOLD HIGH-RESOLUTION O $1s$ PHOTOELECTRON SPECTROSCOPY OF CO₂

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The O $1s$ ionization spectra of CO₂ are dominated by the $5\sigma_g^*$ and $4\sigma_u^*$ shape resonances, centered at ~ 2 and ~ 20 eV above the O $1s$ ionization threshold [1]. If one adopts one-particle description, valence electrons can be regarded as independent spectators in the excitation of the O $1s$ electron to the $5\sigma_g^*$ and $4\sigma_u^*$ molecular orbitals. Double excitations and changes in nuclear motion, however, often accompany the inner-shell excitations and open questions to the validity of the one-particle description [2]. In the present study we focus on O $1s$ photoemission at the $5\sigma_g^*$ shape resonance just above the threshold.

Coupling between the slow photoelectron and the nuclear motion is an intriguing theoretical problem because in molecular species, in addition to the post-collision interaction [3] (PCI) among photoelectrons, Auger electrons and ions, the coupling between the photoelectron and vibrations in the residual singly charged ion are also present. The calculations are based on the quasi-atomic and optical potential concepts [2] that allow us to predict essential contribution of the quasi-elastic component to the photoelectron band, such as population of high vibrational components and non-Franck-Condon distribution of the vibrational branching ratios, as well as asymmetry parameters β of these vibrational components.

Experimentally, we collected for the first time angle-resolved O $1s$ photoelectron spectra of CO₂ in the region of the $5\sigma_g^*$ shape resonance. Experiments were carried out on beamline 27SU at SPring-8 using a high-resolution electron spectrometer (Gammadata-Scienta SES2002). The present high-resolution ($\Delta E \sim 140$ meV) allows us to resolve the vibrational structure, which is dominated by the progression of the antisymmetric stretching mode (313 meV separation), that becomes allowed due to symmetry breaking [1]. Vibrational branching ratios and asymmetry parameters β are extracted from the present data by fitting the spectra with PCI-distorted lineshape [3]. The present results show significant non-Franck-Condon behaviour of the branching ratios and essential changes in asymmetry parameters β across the $5\sigma_g^*$ shape resonance. Semi-quantitative agreement between the measurements and calculations are found.

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DEFORMATION OF O1s EXCITED N₂O STUDIED BY MOMENTUM MEASUREMENTS OF FRAGMENT IONS

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The equivalent-core model predicts that N₂O in the O1s⁻¹3π* state is bent. The equilibrium bond angle of N₂O in the O1s⁻¹3π* state is calculated to be 111.7 degrees. The angular distributions of fragment ions from N₂O in the O1s⁻¹3π* state also suggest that the molecule is bent [1,2]. We measured the momenta of three fragment ions (N⁺, N⁺, and O⁺) from N₂O³⁺ following O1s→3π* photoexcitation in N₂O, in order to clarify how the molecule deforms at the π* resonance. The experiments were performed on the c-branch of BL27SU at SPring-8. The momenta of three fragment ions were measured in coincidence using a time-of-flight mass spectrometer fitted with a position sensitive detector and a supersonic jet of N₂O. Figure 1 shows the distributions for the angle between the momenta of the terminal N⁺ and the O⁺ ions for the triple fragmentation (N_t-O angle) through the O1s→3π* resonance (solid circles) and the O1s→3sσ* resonance (open circles). Ions are collected for emission over 4π steradian. Because only the simultaneous three-body break-up contains information about the geometry of the parent ions, in the off-line analysis we selected only these events, rejecting those where the fragmentation proceeds via sequential steps. The N_t-O angle distribution at the O1s⁻¹3sσ* state is peaked at about 165 degrees. This angle corresponds to the angle due to the ground-state zero-point vibration. The N_t-O angle distribution through the O1s→3π* excitation shows a broad peak centered at about 162 degrees, with a long tail towards lower angles. The comparison between the two angle distributions clearly shows that the molecule is more bent at the O1s⁻¹3π* state than at the O1s⁻¹3sσ* state.

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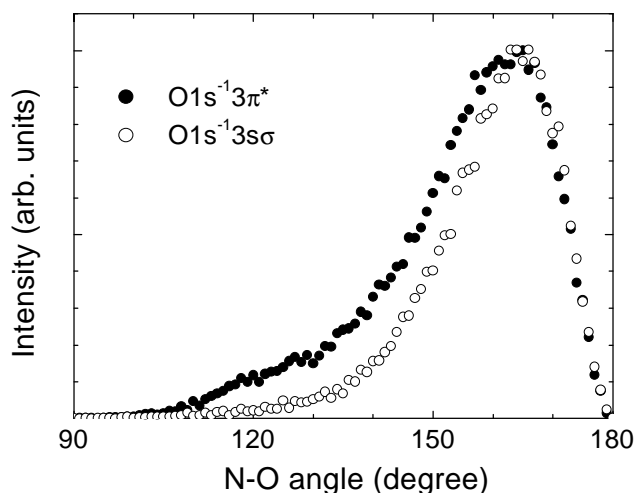


Figure 1. The distributions for the angle between the momenta of the terminal N⁺ and the O⁺ ions for the triple fragmentation through the O1s→3π* resonance (solid circles) and the O1s→3sσ* resonance (open circles).

THE PHOTOABSORPTION CROSS SECTION OF Kr IN THE SUB keV ENERGY REGION

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It is important to obtain reliable data on photoabsorption cross sections of rare gas atoms in detail for clarification of fundamental interaction between photon and material. However, there are limited number of data reported about those cross sections in the soft X-ray region [1-3]. We report here the precise photoabsorption cross section for Kr in the soft X-ray region using a multi-electrode ion chamber [4]. The spectral purity of monochromatized synchrotron radiation was improved through the low energy operation of the storage ring (TERAS) and through inserting a thin metal foil into the incident photon beam. The ion chamber includes 4 electrodes for collecting photoions. The length of the two electrodes mounted near the entrance window is 100mm and that of the other two is 500 mm. The measurement using the electrodes with different lengths enables us to remove the contribution of the stray light and higher orders in the photoion-currents, as follows. The photoion-current (i) of the electrode from the 1st order light is given by the following equation.

$$i = enI \exp(-dp\mathbf{s})(1 - \exp(-Lp\mathbf{s})). \quad (1)$$

In this equation, I , e , n , d , L , p , and \mathbf{s} denotes the incident photon intensity, the elementary charge, the number of electrons totally produced from a photon in the chamber, the length of insensitive region in front of the electrode, the electrode length, the gas density, and photoabsorption cross section, respectively. The photocurrents from the stray and higher orders are also given by Eq.(1) with different I , n , and \mathbf{s} . The photoabsorption cross section is obtained by fitting Eq.(1) to the photocurrents of the 4 electrodes measured with several gas densities, which include contributions from the first order light, stray and higher orders. Figure 1 shows the photoabsorption cross section of Kr in the region of 80 eV to 1200 eV, together with literature data [1,3]. Although the present results are close to the reported values, there are seen some discrepancies between the previous data and the present ones.

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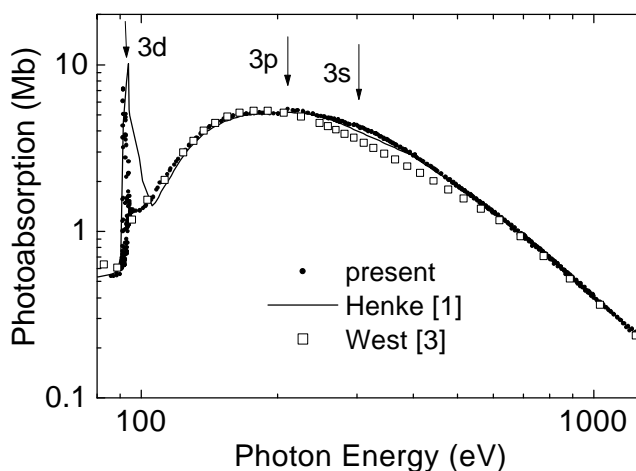


Figure 1 Photoabsorption cross section of Kr.

W-VALUES OF RARE GAS ATOMS IN THE SUB keV X-RAY REGION

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The W-value is defined as average energy required to produce an electron-ion pair in a gas system by ionizing radiation. This value is a fundamental constant regarding interaction between the radiation and an atom and/or a molecule. Above several keV, the W-value is insensitive to quality and energy of the radiation. On the other hand, this value for low-energy radiation varies around the inner-shell ionization threshold of the atom [1]. In the present study, photon W-values for rare gas atoms have been obtained in an absolute scale in the region of 90-1000 eV using a multiple electrode ion chamber.

Synchrotron radiation from the TERAS electron storage ring was dispersed using a Grasshopper monochromator. Thin filters and low energy operation of the ring were used for improving spectral purity [2]. Monochromatic soft X-rays entered the ion chamber, and then ions produced in the chamber were collected with electrodes, and these photoion currents were measured as a function of the gas density.

The photon W-value, W_p , is given with

$$W_p = E_p / N \quad (1)$$

In this equation, N denotes the number of electrons totally produced in the sufficiently voluminous gas system and E_p is the photon energy. The number of electrons, n , totally produced under a gas density of p , is the summation of the initial ionization and the secondary ionization effects in the chamber.

$$n(p) = g + d(p). \quad (2)$$

In eq.(2), g denotes the number of electrons ejected from the atom absorbing a photon, and d is the number of electrons secondarily produced through the collision between ambient atoms and emitted electrons. Photon W-values have been determined from ion currents at sufficiently low and high gas densities in the ion chamber. Figure 1 shows photon W-values of Kr in the soft X-rays region (solid circles). The photon W-value shows a peak just below the Kr 3d ionization threshold, increases steeply just above this threshold and becomes nearly constant in higher energies. The open squares indicate data of the W-value for electrons. The solid curve denotes the result derived from a model here proposed, which takes into account atomic shell effects in the initial photo-ionization step.

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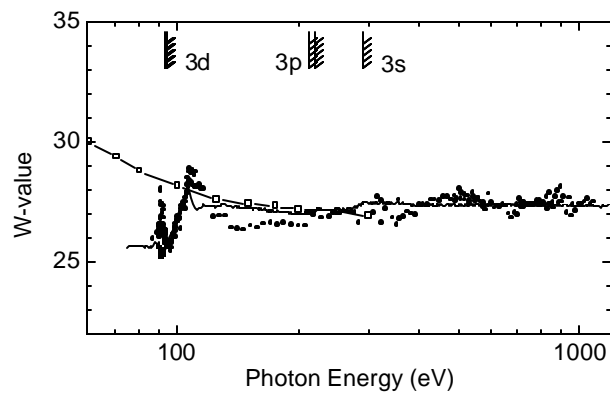


Fig.1: Photon W-value of Kr.

FINE-STRUCTURE SELECTIVITY OF NEUTRAL DISSOCIATION OBSERVED IN O₂

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The knowledge about the decay mechanisms of superexcited states - states whose internal energy exceeds the lowest ionization energy - is presently far away from being complete [1]. Superexcited states have several possible decay paths such as formation of electrons and molecular ions through autoionization and of neutral atoms through dissociation where their internal energy is distributed among the arising fragments. If a neutral fragment emerges from the dissociation process in an excited state which can decay further by fluorescence, photon-induced fluorescence spectroscopy (PIFS, see, e.g., [2]) - measuring the exciting-photon energy dependence of the fluorescence spectrum - can be applied.

Synchrotron radiation from BESSY I, Berlin, was monochromatized by a 3m-normal-incidence monochromator (3m-NIM-2) equipped with a 2400 lines/mm grating and focused into a liquid nitrogen cooled target gas cell. The target cell contained molecular oxygen at a pressure of 40 μ bar. For detecting the atomic fragment fluorescence a VUV-photomultiplier with a CsI coated photocathode and a MgF₂ entrance window was used. The exciting-photon flux transmitted through the gas cell was monitored and enabled to determine the absorption cross section simultaneously with the fluorescence spectrum of the dissociation fragment as a function of the exciting-photon energy. For slit widths of 20 μ m a bandwidth of the exciting radiation of 0.9 meV was achieved. The exciting-photon energy was varied from 14.6 eV to 16.3 eV in steps of typically 0.2 meV.

The absolute O₂ absorption cross section and the absolute emission cross section for OI (⁴S^o)3s ³S₁^o → 2p⁴ ³P_J were investigated using PIFS in the vicinity of the threshold for neutral dissociation leading to the OI (⁴S^o)3s ³S₁^o state with a very narrow bandwidth (0.9 meV) of the exciting radiation. Both cross sections are found to be structured by the vibrational progressions of the O₂ Rydberg states I, I' and I'' which converge to the a ⁴Π_u state of O₂⁺. In the present investigation the fine-structure components of the vibrational progressions of the I, I' and I'' states were resolved for the first time in a fluorescence excitation spectrum. A certain degree of selectivity in the population of fine-structure components was observed in the fluorescence excitation spectra.

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AUGER ELECTRON SPECTRA OF Kr2p HOLES USING MONOCHROMATIC SOFT X-RAYS

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Radiationless transitions are of great interest because of the dominant mode for de-excitation of atomic inner-shell vacancies and of the main factor for determining hole-state lifetimes [1-3]. Rates and energies of Auger and Coster-Krönig transitions provide stringent tests of theoretical models on electronic coupling, correlation and relativistic effects. Auger electron spectra from Kr2p hole states were studied using techniques of electron beam excitation and of ion beam excitation [1-2], and then they were compared with results calculated by several theoretical methods. Since experimental data were obtained at a moderate resolution, however, there has been obtained no clear conclusion on branching ratios for the multiplet final states populated densely. In the present study normal Auger spectra of 2p holes have been measured using monochromatized synchrotron radiation and a high resolution electron spectrometer.

Measurements were performed in the c branch of the undulator beamline 27SU at SPring-8. Ion yield spectra were measured in the region of the ionization thresholds of Kr2p electrons for confirming the energy of the incident photon beam. Electrons emitted from the sample gas were observed at the direction parallel to the photon polarization with the hemispherical electron energy analyzer (SES 2002). Auger spectra of $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ are shown at the upper part and the lower in Fig. 1, respectively. Thin dotted curves denote peaks calculated for individual final states using Gaussian and Lorentzian shapes for instruments and lifetime widths. Thick curves are the summation of all thin curves. It is seen that the present result has been obtained with the resolution higher than the reported data [1-2]. Energies for the spectral peaks here obtained agree with the previous results at most final states. However relative intensities for several peaks are appreciably different from the reported ones.

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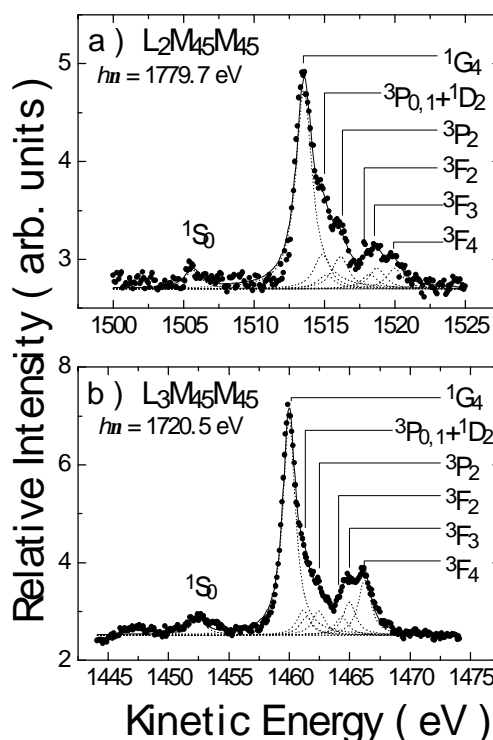


Fig.1: Photoexcited Auger electron spectra of Kr.
a) $L_2M_{45}M_{45}$, b) $L_3M_{45}M_{45}$

EXPERIMENTAL STUDIES AND *AB INITIO* CALCULATIONS ON CHARACTERISTICS OF THE C STATE OF SF₂ RADICAL

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SF₂ radicals were generated by a pulsed *dc* discharge in the mixture gas beam of SF₂ and Ar. The (2+1) resonance-enhanced multiphoton ionization (REMPI) excitation spectroscopy of SF₂ radical was obtained between 325 and 365 nm. The SF⁺ ion signals were also observed in the same wavelength range. These results are shown in Fig.1. The excitation spectrum of SF₂ can be assigned a two-photon resonant transition from the ground state to *B*¹*B*₁(4s) Rydberg state and *C* state.

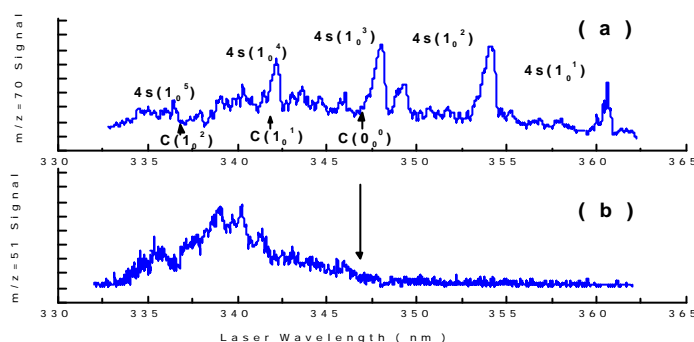
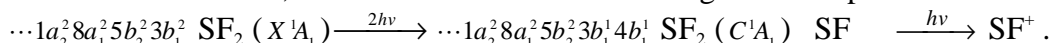


Fig. 1 Composite (2+1) REMPI excitation spectrum between 330 and 365 nm, which were carried by a) SF₂⁺ (m/z 70) and b) SF⁺ (m/z 51)

Ab initio calculations were carried out using GAUSSIAN98 programs. The optimized geometries, harmonic vibrational frequencies, excited energies and the PESs of the ground state and several excited states of SF₂ calculated at CIS/Aug-cc-PVTZ. It is reasonable to assign the second ¹*B*₁ state as the *B*¹*B*₁(4s) Rydberg state, and the ¹*A*₁ state as the *C* state in experiment. It also shows that the *B*¹*B*₁ states of SF₂ radical are a bonding state and the *C*¹*A*₁ state is a valence state with predissociative characteristics, which are in agreement with experiment.

As shown in Fig.1, SF₂⁺ and SF⁺ signals can be observed in the same wavelength. The trace of SF⁺ began at 350 nm, close to the band origin of the *C* state. According to our experiments and calculations, we think that the *m/z* 51 signal originates from the REMPDI processes. That is, the *C*¹*A*₁ state derives from the ground state by two-photon resonant excitation, then dissociates to the neutral SF radical, which can ionize after absorbing one laser photon:



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FRAGMENT-ION DESORPTION FROM SULFUR-CONTAINING AMINO ACIDS BY LOCALIZED CORE-LEVEL EXCITATION

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Irradiation of VUV or X-ray on solid surface induces decomposition and desorption triggered by the core-level excitation. Due to the localized nature of core levels, many examples for site-specific and element-specific reactions have been reported. Generally, such specific reaction is clearly observed in thin films of adsorbed molecules. In condensed phase or bulk materials, the specificity is weakened due to the secondary electrons which induce non-specific reaction. Here we present clear examples where the localized core-level excitation in bulk biological molecules induces desorption of specific fragment ions.

The molecules investigated are sulfur-containing amino acids, such as cystine, cysteine and methionine. The fragmentation pattern in these molecules by the core-level excitation is of great importance in elucidating the effect of radiation on living things [1]. The samples were pressed into pellets, and irradiated in ultra-high vacuum by synchrotron beam around the sulfur K-edge. The desorbed ions were detected in-situ by a quadrupole mass spectrometer. For comparison, the desorption of fragment-ions by valence excitation was measured using low-energy electron gun. The photoelectron and Auger electron spectra were also measured by a hemispherical electron energy analyzer.

For valence excitations, various fragment ions containing carbon, nitrogen and oxygen were desorbed, but the core-to-valence resonant excitations at the sulfur K-edge induced only S^+ ion desorption. Figure 1 shows the photon-energy dependencies of the total electron yield (TEY) and S^+ ion yield for cystine which has a disulfide bond. When we compare the jump ratio (I_{on}/I_{off}) defined as the peak intensity ratio between off-resonance and on-resonance energies, the I_{on}/I_{off} ratio for the TEY curve is 1.5, but the value for the S^+ yield curve exceeds 20. The results clearly show that the S^+ desorption is caused not by the secondary electrons but the direct core-to-valence resonance localized at the sulfur atom. As to the photon-energy dependencies, the TEY curve exhibits the double structure of the $S\ 1s \rightarrow \sigma^*$ resonance peak, corresponding to the excitations into the σ^* state localized at the S-S bond (peak A) and that localized at the S-C bond (peak B) [2]. While the S^+ yield curve has single structure around the peak A. The results also suggest that the direct core-to-valence resonant excitation localized at the S-S bond has high efficiency for the S^+ desorption. The mechanism of desorption is discussed on the basis of the photoelectron and Auger electron spectra.

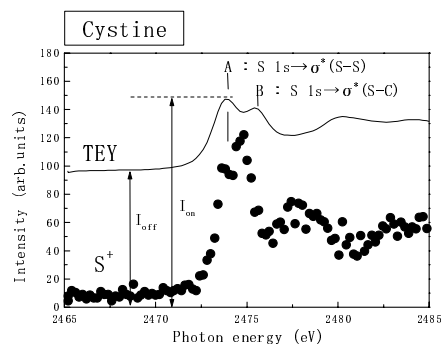


Figure 1: Photon-energy dependencies of the TEY and S^+ yield around S K-edge for cystine.

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MOLECULAR SIZE EFFECT ON THE SITE SPECIFIC FRAGMENTATION OF THE N AND O K-SHELL EXCITED $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{CN}$ ($n=0, 1, 3$) MOLECULES

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Site specific photofragmentation following the innermost 1s electron has been investigated in expectation of a possibility that a chemical bond fission will be localized around the atomic site of excitation of a molecule [1]. We anticipate that the site specific photofragmentation may depend on the molecular size. In the present work we employed a series of $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{CN}$ ($n = 0, 1, 3$) molecules since they have the CO and CN groups.

The experiments were performed on the beamline BL8B1 at the UVSOR of IMS. A reflectron-type TOF mass spectrometer was installed in the main chamber that was rotatable from -20 to 110 degrees with respect to the linearly polarized electric vector of synchrotron radiation. In this work it was fixed at the magic angle. Figure 1 shows the TOF mass spectra of CH_3COCN and $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CN}$ excited at the $\pi_{\text{CN}}^* \leftarrow \text{N}(1s)$ and $\pi_{\text{CO}}^* \leftarrow \text{O}(1s)$ resonance transitions. We see that the site dependent fragmentation is small or negligible in the small CH_3COCN and $\text{CH}_3\text{COCH}_2\text{CN}$ (not shown) molecules. The site specific photofragmentation was clearly observed in the long-chained $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CN}$ molecule: At the terminal N(1s) excitation many small fragment ions were produced and at the O(1s) excitation the main product was CH_3CO^+ fragment. The observed site specific fragmentation seems to be related to the shape of the valence orbital of bonding electrons.

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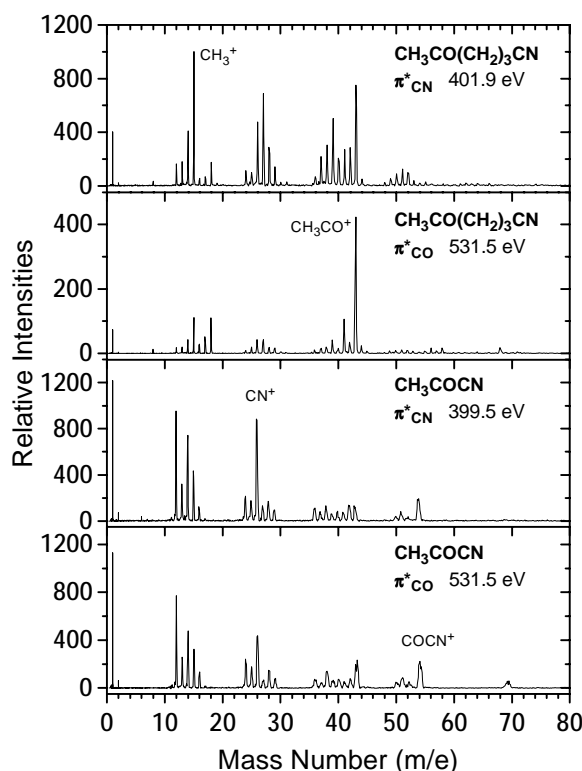


Figure 1. Reflectron-type TOF mass spectra of CH_3COCN and $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CN}$ molecules excited at the O and N K-shells.

RESONANT AUGER SPECTRA OF Kr NEAR THE L_3 THRESHOLD

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The 2p electron of krypton can be excited into the vacant 5s orbital [1]. The resonant Auger electron spectrum following photoexcitation to the 5s level was first observed by use of a cylindrical-mirror-type electron analyzer [2]. However, assignment of the final states is open for question, because a low resolution was employed. In the present work we measured the Auger electron spectra in the energy region crossing the $\text{Kr}(2p) \rightarrow 5s$ resonance excitation by using a high resolution analyzer (SES 2002). Measurements were performed on the undulator beamline BL27SU of SPring-8.

Figure 1 shows the Auger spectrum of $L_3\text{-}M_{45}M_{45}5s$ transition at $h\nu = 1677.3$ eV. The final states were assigned from Ref. 3. The dots are the experimental data, the thin curves denote the peaks for individual final states, and the thick one is the sum of the thin curves. The Auger peaks shifted linearly with the photon energies as are expected. The intensity of 1G_4 peak increased with photon energy and that of the $^3P_{0,1}+^1D_2$ peak was maximum at the $\text{Kr}(2p) \rightarrow 5s$ resonance excitation.

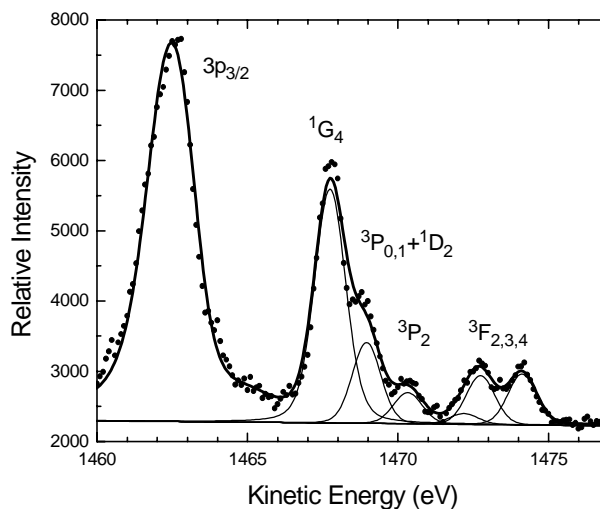


Figure 1. Resonant Auger spectrum of $L_3M_{45}M_{45}5s$ of Kr.

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ANGLE-, ENERGY-, AND MASS-RESOLVED PHOTOFRAGMENTATION OF THE C AND N K-SHELL EXCITED CF₃CN MOLECULE

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Inner-shell photoexcitation dynamics of trifluoroacetonitrile (CF₃CN) is of great interest because the C–C≡N skeleton is linear in the ground state. In addition, fluorine is the most electronegative atom and induces the largest chemical shift around it in a molecule. Thus, we can selectively excite the *K*-shell electron of either carbon atom besides the N(1s) of CF₃CN.

Measurements of the angle-resolved time-of-flight (TOF) mass spectra were done on the beamline BL8B1 at UVSOR facility. First, photoabsorption spectra were observed at room temperature in the C and N *K*-shell regions. The TOF mass spectra were then measured at the several prominent resonance peaks observed. The spectra were acquired at 0° and 90° angles with respect to the linearly polarized electric vector of the incident photon. Figure 1 shows the enlarged TOF mass spectra recorded at the $\pi^* \leftarrow C_N(1s)$ resonance excitation of CF₃CN. It is noteworthy that the peaks of CN⁺ and CF₃⁺ observed at the 90° angle distinctly split into triplets. The profiles of CN⁺, CF⁺, and CF₃⁺ peaks were reproduced by the fitting method developed by Saito and Suzuki [1] to obtain the angular distributions of the energetic photofragment ions. The CN⁺ and CF₃⁺ ions are produced by typical Π – Σ transition, which means that the symmetry basically holds also for the relatively large CF₃CN molecule. The anisotropy parameters for CN⁺ were found to be +0.10, -0.57, and -0.85 for kinetic energies 0.01–0.41, 0.67–3.61, and 4.33–6.86 eV, respectively. More distinct results were obtained for the N(1s) excitation.

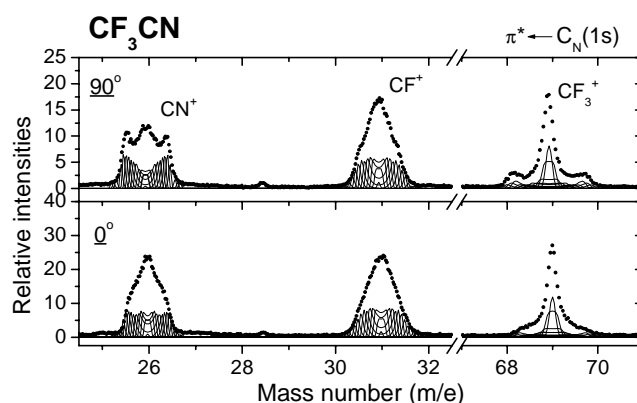


Figure 1: Experimental and simulated angle-resolved TOF mass spectra recorded at the $\pi^* \leftarrow C_N(1s)$ resonance excitation of CF₃CN. The solid curves are the simulated profiles for the kinetic energy components of 0.01–6.86, 0.01–6.86, and 0.01–3.17 eV for CN⁺, CF⁺, and CF₃⁺ ions, respectively.

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SYMMETRY BREAKING OF SiF₄ MOLECULE BY F 1s EXCITATION

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The lifetime of the core-excited state of a molecule consisting of light atoms (C, N, O, and F) is $> 10^{-15}$ s and thus nuclear motion in the molecular core-excited state can proceed before the Auger decay. The angular distribution measurement of the fragment ions provides us with information not only on symmetries of the core-excited states but also symmetry breaking due to asymmetric nuclear motion in the core-excited states. In the present study we have investigated the angular distribution of the fragment ions ejected after F 1s excitation of the SiF₄ molecule to probe the symmetry breaking by the F 1s excitation.

The experiments were performed on the soft X-ray photochemistry beamline BL27SU at SPring-8. Using a pair of energetic ion detectors of retarding-potential type mounted in the direction parallel (0°) and perpendicular (90°) to the polarization vector, we measured yield curves of energetic ions (F⁺ with $KE \geq 6.4$ eV) of SiF₄ in the F 1s excitation region. We also measured the total ion yield (TIY) curve simultaneously.

Figure 1 shows the total and energetic ion yield spectra of SiF₄ in the F 1s excitation region. The peak at 689.2 eV is clearly separated from other structures in the present spectra, while it appeared as a shoulder structure in ref. [1]. We can clearly see anisotropic angular distributions of the F⁺ energetic fragment ions, suggesting the symmetry breaking in the F 1s core-excited state. This result can be interpreted as the localization of the valence holes produced by Auger decay of the F 1s core-hole state, as in the case of SF₆ [2] and CF₄ [3].

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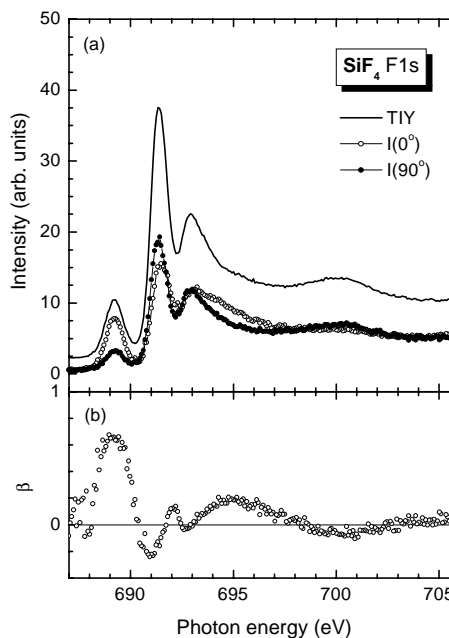


Figure 1: The yield spectra and the anisotropy parameter β of photofragment ions of SiF₄ in the F 1s excitation region.

PHOTODOUBLE IONIZATION OF D₂ AND He WITH ASYMMETRIC KINEMATIC CONDITIONS

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Following on from the first molecular ($\gamma, 2e$) ‘triple’ differential cross section (TDCS) measurements for D₂ [1], with equal energies for the two ejected electrons ($E_1 = E_2$), we present mutual angular distributions for $E_1 \neq E_2$. These photodouble ionization (PDI) studies were performed at the Super-ACO synchrotron source (Orsay, France) using a dual-toroidal electron-electron coincidence spectrometer [2] and full details are available in [3]. Measurements taken using helium under near-identical conditions are also presented for comparison. Both targets were excited to 25 eV above their PDI thresholds (79.00 and 51.17 eV for He and D₂, respectively) using linearly polarized light ($S_1 = 0.9 \pm 0.05$, $S_3 = 0$). Mutual angular distributions were recorded between electrons with energies of 5 and 20 eV. The results for $\theta_1 = 0^\circ$ and 90° are shown in Figure 1, where θ is measured relative to the electric field direction.

The helium TDCSs are in excellent agreement with recent ‘hyperspherical R -matrix with semiclassical outgoing waves’ (HRM-SOW) calculations [4]. The D₂ results have similar features to those of He, yet there are some significant differences. Of most interest is the suppression of the back-to-back maximum for $\theta_1 = 0^\circ$ (Figure 1b) which could be evidence of interference effects arising from the two center nature of the target.

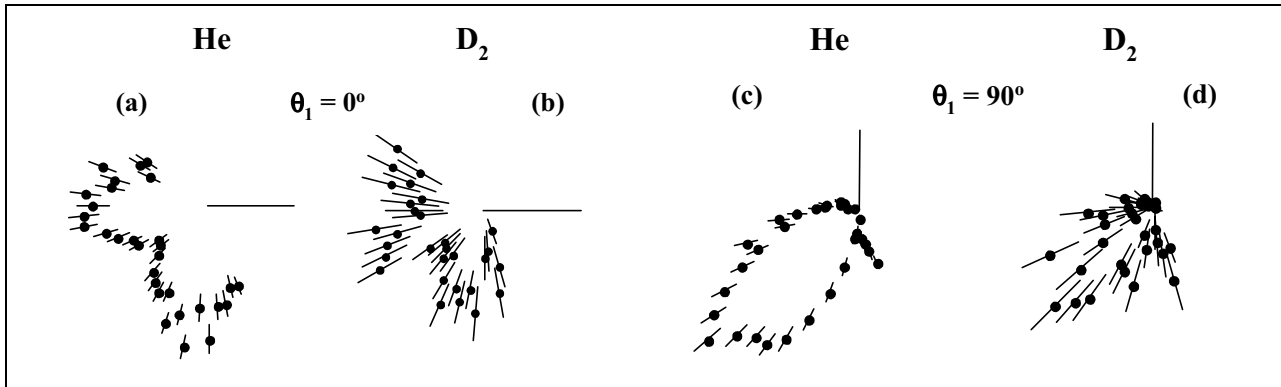


Figure 1. ($\gamma, 2e$) triple differential cross sections for He (a,c) and D₂ (b,d) on an arbitrary scale. The reference electron has an energy (E_1) of 5 eV and E_2 is 20 eV; in all case the data points are plotted in 5° intervals. The scatter is generally greatest at $\theta_2 \sim 270^\circ$ due to a minimum in the argon coincidence spectrum used for normalization.

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PHOTOIONIZATION OF ATOMIC TITANIUM

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The 3p multiplet structure of the photoelectron spectra for the 3d metal atoms is dominated by the Coulombic 3p-3d interaction due to the large overlap of the 3p hole state and the (collapsed) 3d wave functions of the valence electrons. Previous experiments on heavier 3d metal atoms [1,2] have shown that the subsequent Auger decay has a distinct influence on the linewidth of the different components giving rise to a near suppression of the so-called low-spin components.

The 3p⁻¹ photoelectron spectra of the free Titanium atoms has been recorded using a high resolution Scienta electron analyzer and the synchrotron radiation from the high-brilliance light source Bessy II. For the understanding of the 3p ionization of Ti not only the term-dependent linewidth of the different multiplet states, but also shake-up satellites and the influence of the nearby 3s ionization must be considered.

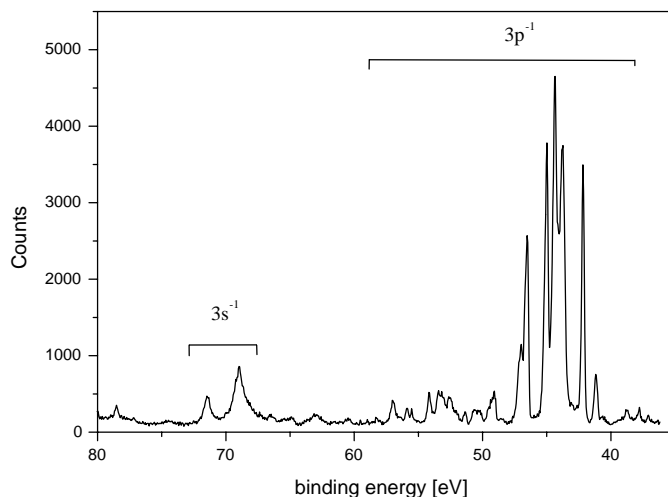


Figure 1: Photoelectron spectrum of atomic Titanium, $h\nu = 110$ eV.

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NEUTRAL DISSOCIATION OF MOLECULAR OXYGEN BY VUV RADIATION

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The neutral dissociation of molecular oxygen excited by synchrotron radiation was studied experimentally and theoretically. The experimental setup was as described previously [1].

The energy of the exciting photons was varied in the interval 20.8-24.8 eV which corresponds to excitation of the $2\sigma_u^{-1}(c^4\Sigma_u^-)n\sigma_g$ Rydberg states. The absolute value of the

photoemission cross section for atomic fragment fluorescence in the detection range from 97 nm to 131 nm was measured for the first time. The measured cross section is shown in figure 1 in comparison with the photoabsorption cross section from [2].

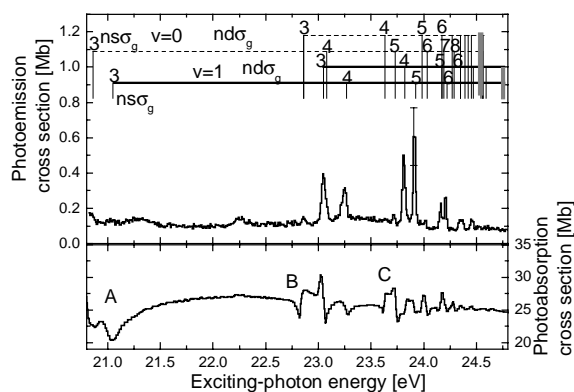


Figure 1: Measured photoemission and photoabsorption cross sections of O_2 . The potential curves from [3].

To understand why some features observed in the photoabsorption cross section, *e.g.*, the peaks A, B and C, are suppressed in the photoemission cross section, the Auger rates for the $2\sigma_u^{-1}(c^4\Sigma_u^-)n\sigma_g$ Rydberg states were calculated as well as the dissociation lifetimes τ_{dv} . The τ_{dv} values were computed using the

The calculations showed that the τ_{dv} for the first vibrational level $v=0$ is equal to $3.4 \cdot 10^{-12}$ s and significantly larger than the Auger lifetime ($3.3 \cdot 10^{-15}$, $1.6 \cdot 10^{-14}$, $3.3 \cdot 10^{-14}$ s for the first three Rydberg members, respectively). As a consequence, the levels corresponding to $v=0$ decay by emitting an Auger electron rather than by dissociation and are invisible in photoemission. The dissociation lifetime of the $v=1$ level is equal to $6.3 \cdot 10^{-14}$ s and thus small enough to explain the features observed in the photoemission cross section.

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COMPETITION OF SINGLE- AND DOUBLE-EXCITATION PROCESSES IN THE THRESHOLD PHOTOIONIZATION OF FREE ATOMS.

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High-resolution study of the photoionization (PI) of outer shells of noble-gas atoms is the subject of a long-standing interest starting from the work [1]. The reason lies in a variety of resonant pathways of the PI which manifest themselves as prominent autoionization profiles appearing on the smooth background of the non-resonant PI cross section (CS).

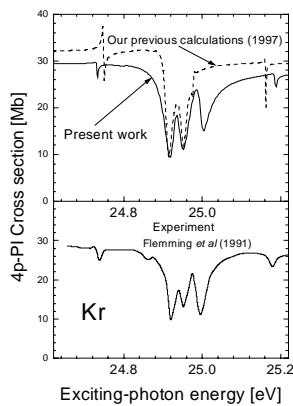


Figure 1: Comparison of calculated and measured Kr 4p-PI CS.

During the last years considerable progress has been achieved in the study of the $3s$ - np isolated resonances in the $3p$ -PI of Ar and Ar-like ions (see, e.g., [2,3]). In the excitation energy region above the $3s$ -threshold the resonance structure is more complex [3-5]. It is caused by the $3p^6$ - $3p^4nl n'l'$ double-electron excitations.

In the case of Kr the mixing of the singly and doubly excited resonance states leads to a complex structure of the $4p$ -PI already in the region of $4s$ - np resonances. The measured $4p$ -PI CS in the region of the first $4s$ - $5p$ excitation [6] is presented in the lower part of figure 1 for comparison. The first theoretical interpretation of the resonant structure was given in our previous work [5] and is presented as a dashed line in the upper part of the figure. However, due to the considered limitations of the computational model the agreement between the calculated and measured shapes of the resonances was still incomplete.

In the present work extended calculations were performed. The new results are presented in the upper part of figure 1 as a solid line. The good agreement obtained shows that the following effects play an important role and should be incorporated in calculations:

- the interactions between resonances via the decay continua;
- the interaction between different continua, which was accounted for by using the K-matrix technique;
- the core polarization by the doubly-excited electrons.

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Dissociative single and double photoionization of CF_4 and ionic fragmentation of CF_4^+ and CF_4^{2+} in the range from 23 to 120 eV

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We have studied dissociative single and double photoionization processes with time-of-flight mass spectrometry and the photoion-photoion-coincidence (PIPICO) method by use of synchrotron radiation in the photon energy range of 23-120 eV. The TOF mass spectra and the PIPICO spectra were measured at an angle of $\sim 55^\circ$ with respect to the polarization vector where the second-order Legendre polynomial is close to zero. Under these conditions, the effects of anisotropic angular distributions of fragment ions are minimized [1]. To obtain accurate ion branching ratios, the radio frequency (rf) signal of the storage ring was used as the start signal of a time-to-amplitude converter.

The present study focuses on the determination of the ratio of double to single photoionization (σ^{2+}/σ^+) and the partial cross sections for single (σ^+) and double (σ^{2+}) photoionization as a function of photon energy. Second, the ion branching ratios and the partial cross sections for the individual ions respectively produced from the parent CF_4^+ and CF_4^{2+} ions are separately determined. Third, the dissociation ratio of the parent CF_4^{2+} ions into two ionic fragments is determined.

The ion branching ratios and the absolute partial cross sections for the production of singly charged CF_3^+ , CF_2^+ , CF^+ , F^+ , and C^+ ions, as well as doubly charged CF_3^{2+} and CF_2^{2+} ions have been previously reported [2]. The ratio of double to single photoionization was obtained first, increasing monotonically with photon energy. The threshold of double ionization 37.5 ± 0.5 eV is in good agreement with the value 37.6 ± 0.6 eV reported by Codling et al. [3]. Above 100 eV, the ratio exceeds 0.3. Since the total photoabsorption cross section of CF_4 in this photon energy range has been reported [4], the σ^{2+}/σ^+ ratio is converted to the absolute cross sections for single and double photoionization.

Ion branching ratios for the individual ions respectively produced from the parent CF_4^+ and CF_4^{2+} ions are determined separately, thus enabling more detailed study of the dissociation processes of the CF_4^+ and CF_4^{2+} ions. For the ion branching ratios of CF_4^+ , the major ions produced are CF_3^+ and their ratio still increases at higher photon energies. The ratio for C^+ also increases with photon energy up to about 85 eV. As for the fragmentation of CF_4^{2+} , two body dissociation $\text{F}^+ + \text{CF}_3^+$ takes place first. Depending on the number of neutral fluorine atoms in the dissociation, the different channels ($\text{F}^+ + \text{CF}_2^+ + \text{F}$, $\text{F}^+ + \text{CF}^+ + 2\text{F}$, and $\text{F}^+ + \text{C}^+ + 3\text{F}$) appear one after another.

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Fragmentation of doubly charged CF_4^{2+} ion

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The doubly charged CF_4^{2+} ion has received much attention recently by the advent of synchrotron radiation. Recently Hall et al. [1] reported the threshold for double ionization to be 37.5 ± 0.5 eV using threshold photoelectron(s) coincidence (TPEsCO) spectroscopy. Experimental information on the CF_4^{2+} dication has also been obtained via Auger spectroscopy, double-charge-transfer (DCT) spectroscopy, PIPICO, and PEPIPICO experiments. Among these experiments, Codling et al. [2] determined the thresholds for the ion-pair formation of CF_4^{2+} into $\text{F}^+ + \text{CF}_3^+$ (37.6 eV), $\text{F}^+ + \text{CF}_2^+$ (42.4 eV), $\text{F}^+ + \text{CF}^+$ (47.5 eV), and $\text{C}^+ + \text{F}^+$ (62.0 eV) and tentatively correlated these thresholds with specific two-hole states of CF_4 calculated by Larkins and Tulea [3].

In the present study, we have studied dissociative double photoionization processes with the photoion-photoion-coincidence (PIPICO) method by use of synchrotron radiation. The PIPICO spectra were measured at an angle of $\sim 55^\circ$ with respect to the polarization vector to minimize any effects of anisotropic angular distributions of fragment ions [4]. Al optical filter was used to eliminate higher order radiation. The PIPICO branching ratios obtained for these many-body fragmentation channels increase at different photon energies, indicating the existence of fragmentation pathways at these different photon energies. In order to correlate these fragmentation pathways more clearly to the electronic states of CF_4^{2+} , the PIPICO branching ratios for these fragmentation channels were differentiated with respect to the photon energy.

Larkins and Tulea [3] have calculated the energy of the 107 two-hole states associated with the seven outermost orbitals. The electron configuration of the ground electronic state of CF_4 is $(1a_1^2 1t_2^6)(2a_1^2)(3a_1^2 2t_2^6)(4a_1^2 3t_2^6 1e^4 4t_2^6 1t_1^6)$; 1A_1 . The important bonding orbitals are $4t_2$, $4a_1$, $2t_2$, and $3a_1$ [2]. In the attempt to correlate initial states of the CF_4^{2+} ion with the above thresholds for fragmentation, Codling et al. [2] used various simplifying assumptions: the first one is that no fragmentation occurs where both orbitals are non-bonding or antibonding ($1t_1$, $1e$, $3t_2$), and they shifted the calculation of Larkins and Tulea by 4.8 eV. We follow their treatment. The results show that the three-body fragmentation occurs in a relatively narrow energy range from the threshold to about 49 eV, where 14 two-hole states, $1t_1$, $4t_2(2)$; $3t_2$, $4t_2(7)$; $1e$, $4t_2(2)$; $4a_1$, $1t_1(2)$; and $4a_1$, $4t_2(1)$ lies. The value in the parentheses represents the number of the states in this range. That is, only the outer-valence electrons are involved. The four-body fragmentation takes place in a rather wide energy range from the threshold to about 73 eV, where both inner-valence and outer-valence electrons are involved.

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Molecular and dissociative single and double photoionization of CS₂

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Molecular and dissociative single and double photoionization processes of carbon disulfide have been studied with time-of-flight (TOF) mass spectrometry in the 20-120 eV range by the use of synchrotron radiation. The experimental details can be found elsewhere [1]. The observed ions are CS₂⁺, S₂⁺, CS⁺, S⁺, C⁺, and CS₂²⁺. The ion branching ratios for these ions increase at various photon energies, indicating the presence of dissociation pathways at these photon energies. In order to correlate these dissociation pathways more clearly to the electronic states of CS₂⁺ and CS₂²⁺, the ion branching ratios for these ions were differentiated with respect to the photon energy. These differential spectra are similar by nature to those measured by threshold photoelectron-photoion coincidence spectroscopy (TPEPICO) except for a low spectral resolution of the present spectra.

The first peak in the photoion spectrum (dBR/dE) for CS⁺ indicates that the C state of CS₂⁺ dissociates into CS⁺ (and also into S⁺) in agreement with previous observation. The satellite bands due to configuration interaction have been observed in the 19.1-35 eV range by Carnovale et al. [2]. The first peak covers the lower part of the satellite bands, meaning that the lower part of the satellite bands dissociates into CS⁺. The threshold for formation of the metastable CS₂²⁺ ions lies at 27.05±0.02 eV measured by TPEsCO spectroscopy [3]. The second peak locates in the double ionization region, probably indicating that the CS⁺ ions are formed by the charge separation CS⁺+S⁺ of the dication. It is interesting to note that the CS⁺ ions are formed only in a restricted energy range from about 31 to about 42 eV.

The results of the differential spectrum for the CS₂²⁺ ions show that the dication is formed only in a narrow energy range from 27.05 to about 35 eV with a peak at about 29 eV. Hochlaf et al. have reported the potential energy curves along the SC-S coordinate for 14 electronic states of CS₂²⁺ using complete active space self-consistent field (CASSCF) approach and have shown that all low-lying electronic states of CS₂²⁺ are separated by large barriers from their dissociation asymptotes [4]. They have further mentioned that all electronic states up to about 32-33 eV have bound parts on their potential curves and are stable with respect to the dissociation. The present observation is essentially in agreement with their calculation.

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An angular correlation function for double photoionization of an atom using the density and efficiency matrix approach

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We consider the double photoionization process in a rare gas atom as a two-step process, namely (i) photoionization in an inner shell followed by (ii) the emission of an Auger electron from an outer shell. Our treatment makes use of the density matrix approach along with the efficiency matrix which takes care of limitations of the detecting equipment. No reference is made to perturbation theory. Results are obtained for the Xenon atom undergoing photoionization in the $4D_{5/2}$ shell and a subsequent $N_5 - O_{23}O_{23}^1S_0$ Auger transition. Comparison is made with experimental results given by Kämmerling and Schmidt [1] for unpolarized light.

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CASCADE PROCESSES AFTER 3p-SHELL THRESHOLD PHOTOIONIZATION OF Kr

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Inner-shell photoionization of atoms induces sequential vacancy transfer, such as cascades of Auger and Coster-Kronig decays. Multiply charged ions are consequently produced according to steps of the cascades. The branching ratio for channels of the decays can be estimated from yields of the multiply charged ions. In threshold ionization, particularly the branching ratio can be well decided by small disturbances from ionization of other shells.

Multiply charged ions were measured in coincidence with threshold electrons near the 3p-shell ionization limits of Kr. Figure 1 shows yield spectra of total ions, threshold electrons and the multiply charged ions (Kr^{2+} , Kr^{3+} , Kr^{4+} and Kr^{5+}). Peaks at 216 and 223 eV in the yield spectra of the multiply charged ions are due to threshold ionization, in which post-collision interaction effects appear; the profile is asymmetric and broadened [1, 2, 3].

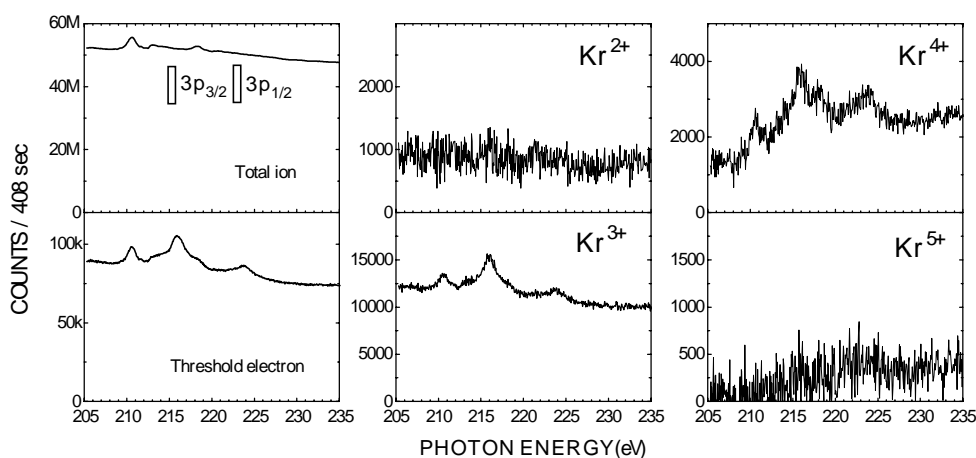


Figure 1: Yields spectra of total ions, threshold electrons and multiply charged ions in coincidence with threshold electrons near the Kr 3p-shell ionization limits.

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STUDY ON THE AUGER ELECTRON CASCADES INDUCED BY PHOTO-EXCITATION OF Kr $3d_j \rightarrow 5p$ AND Xe $4d_j \rightarrow 6p$ ($j=3/2, 5/2$)

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We report the comparison between the experimental results of high-resolution angular distribution measurements and the results of multi-configuration Dirac-Fock (MCDF) calculations for the first-step and the second-step Auger transitions following the photoexcitation in Kr $3d_j^{-1}5p$ and Xe $4d_j^{-1}6p$ ($j=3/2, 5/2$) resonances. The experiment was carried out on the 24-m spherical grating monochromator installed in the soft X-ray undulator beamline 16B at the Photon Factory in Japan using home-made angle-resolved electron spectroscopy apparatus.

The measured electron spectra of the first-step Auger transitions following the Kr $3d_j \rightarrow 5p$ excitation are shown in Figure 1 ($j=5/2$) and Figure 2 ($j=3/2$). Arabic numbers given in the figure correspond to the line numbers given by Mursu et al.[1]. We have obtained values of the angular anisotropy parameter β for the groups of strong lines indicated by roman numbers in Figures 1 and 2. The spectra showed not only the "diagram" lines of the spectator Auger decay but also many of the correlation satellite lines and shake-up satellite lines of the diagram lines. Fairly good agreement between the experimental and the theoretical results for $j=5/2$ excitation have been obtained. Similar results for Xe will also be presented.

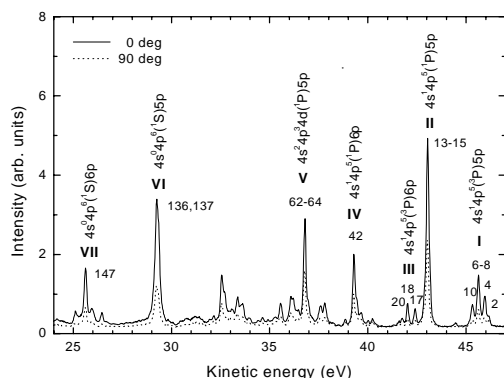


Figure 1: The first step Auger electron spectrum following the Kr $3d_{5/2}^{-1}5p$ excitation.

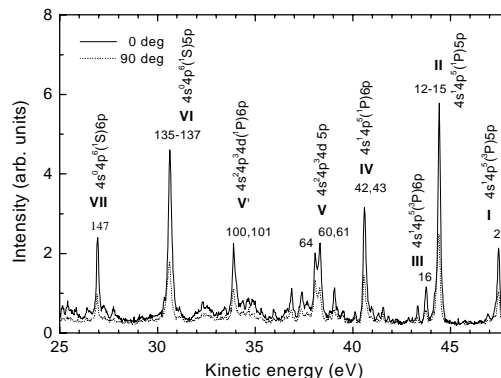


Figure 2: The first step Auger electron spectrum following the Kr $3d_{3/2}^{-1}5p$ excitation.

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POST-COLLISION INTERACTION EFFECTS FOLLOWING 4p-SHELL IONIZATION OF Xe

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Multi-step post-collision interaction (PCI) often occurs in Auger cascades following inner-shell threshold ionization [1, 2, 3]. In the cascades, an initially ejected threshold photoelectron is overtaken sequentially by faster Auger electrons ejected in every step of the cascades. Sudden changes of the Coulomb field due to the overtaking cause the multi-step PCI effect. As a result, the PCI energy distribution for the photoelectron obtains a characteristic profile; the profile is asymmetric and broadened, and its maximum is shifted in energy. Measurements of multiply charged ions in coincidence with threshold electrons enable one to acquire PCI effects divided into the cascades, because multiply charged ions are produced from the cascades following the threshold ionization.

Figure 1 shows yield spectra of Xe^{3+} and Xe^{4+} ions in coincidence with threshold electrons near the 4p-shell ionization limit of Xe. A peak above the ionization limit exhibits the PCI profile.

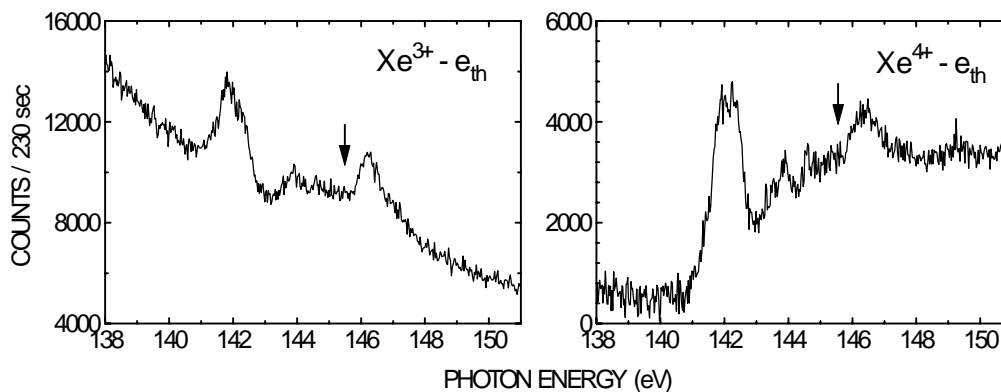


Figure 1: Yields spectra of Xe^{3+} and Xe^{4+} ions in coincidence with threshold electrons near the Xe 4p-shell ionization limit. Arrows indicate the 4p-shell threshold ionization limit.

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RESONANT AUGER SPECTRA OF GAS PHASE KCl

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Normal and resonant Auger spectra of gas phase KCl at the K 2p edge have been measured using synchrotron radiation. The measurements were carried out at beamline I411 at MAX-II laboratory in Lund, Sweden. The beamline is equipped with a Zeiss SX-700 plane grating monochromator. The electron spectra were measured using a Scienta SES-100 analyzer at the magic angle of 54.7° . KCl crystals were evaporated in a resistively heated oven at the temperature of about 600°C under the base pressure of $1.5\text{-}3.3 \times 10^{-7}\text{mbar}$.

Measurements were made as follows: first a total ion yield spectrum at the K 2p edge was measured using a Wiley-McLaren type time-of-flight spectrometer (Figure 1). The spectrum has four distinct maxima that are most likely due to excitations from the K 2p to ms and nd ($m=4, n=3$) Rydberg orbitals [1,2]. Figure 2 displays the Auger electron spectra measured at the two strong resonances ($h\nu=296.75$ and 299.5 eV). Drastic differences seen in the Auger intensity distribution cannot be due to the 2p spin-orbit splitting only, but must be assigned to molecular effects instead. The spectra resemble the results from solid KCl [3], where the orientation of crystal-field-split collapsed 3d orbital was thought to play a crucial role. Similar symmetry considerations could apply in the molecular case.

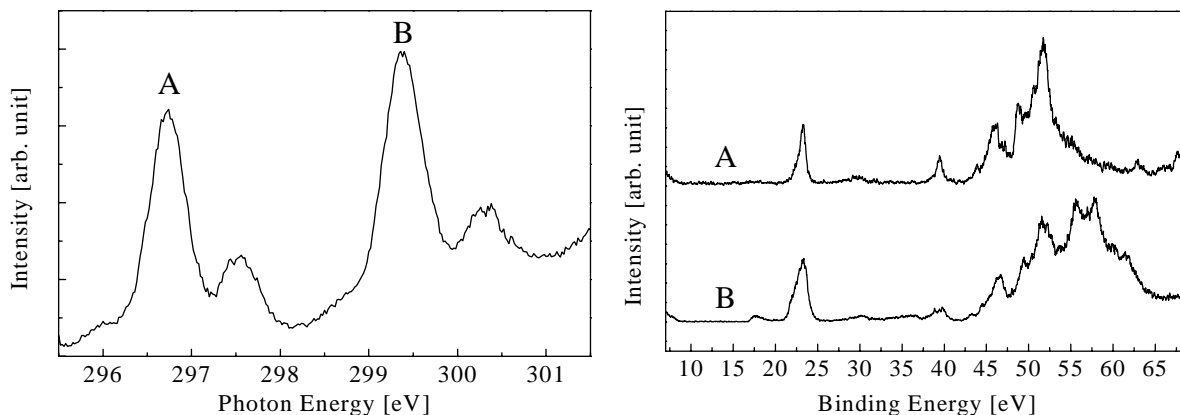


Figure 1: Total ion yield of gas phase KCl.

Figure 2: Auger electron spectra of the KCl molecule.

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DIRECT PROBE OF THE BENT AND LINEAR GEOMETRIES FOR THE CORE-EXCITED RENNER-TELLER PAIR STATES IN CO₂ BY TRIPLE-ION-COINCIDENCE MOMENTUM IMAGING

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The core-excited Π state of a linear molecule CO₂ splits into Renner-Teller pair states A₁ and B₁ (in C_{2v} symmetry) due to vibronic coupling with bending motion. In the present study, we directly measure that A₁ and B₁ states are bent and linear, respectively. The experiment was carried out on the beamline 27SU at Spring-8 in Japan. We employed the triple-ion-coincidence momentum imaging technique, which is based on the time-of-flight method combined with a position-sensitive detector, to extract complete information on the linear momenta of the three ions C⁺, O⁺ and O⁺ produced from the CO₂³⁺ parent ion.

Figure 1 shows Newton diagrams for the three-body break-up of CO₂³⁺ after the C 1s → 2π_u excitation. In these diagrams the amplitude of the linear momentum of the first O⁺ is normalized to unity and its direction is set to negative x, the linear momenta of C⁺ and the second O⁺ are plotted in the positive and negative y directions, respectively. We selected the excitation to the A₁ state selecting the events that eject the C⁺ ion in the direction parallel to the **E** vector and the excitation to the B₁ state selecting the events that eject the two O⁺ ions within the plane perpendicular to the **E** vector. Diagrams (a) and (b) correspond to the selections for the B₁ and A₁ states, respectively. The diagram (a) coincides with those recorded at any other excitation energies, illustrating that the B₁ state is linear: the molecule looks slightly bent in diagram (a), due to zero-point bending motion. In the diagram (b), however, one can recognize a long tail of each island. This tail reflects how much the molecule is bent when it breaks up and thus is direct evidence that the A₁ state is bent.

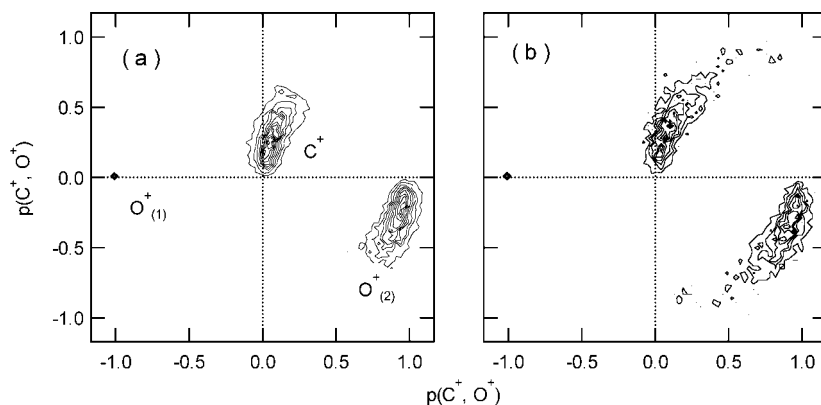


Figure 1: Newton diagrams for the three-body break-up CO₂³⁺ → C⁺ + O⁺ + O⁺ for the C 1s → 2π_u excitation by 290.7 eV photons, (a) to the B₁ state and (b) to A₁.

Electron Beam Ion Trap Spectroscopy of Highly Ionized Tungsten

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In a 1980 Physical Review Letter by Curtis and Ellis [1] an interesting simplification of the lowest excited levels of 61 electron ions was discussed. 61 electron ions belong to the Pm I iso-electronic sequence and the ground configuration of Pm I is $[\text{Xe}]4f^5 6s^2$, which is far from simple. However for higher members of the sequence the 4f orbitals undergo a so-called collapse and the ground state becomes $[\text{Pd}]4f^{14}5s$. The 1st excited levels are then the $4f^{14}5p^2P$ levels and an alkali-like doublet is expected in the spectra. A number of experiments have been attempted to observe this doublet for highly ionized members of the Pm I sequence, for example beam-foil observations of Au. However, in the beam-foil spectra a multitude of lines were observed and only tentative identifications of the Pm-like lines could be given, see [2]. It was suggested in [1] that these doublet lines should be strong in the spectra of plasmas containing such elements. As Tungsten is of current interest in Tokamak fusion plasmas there is an interest in identifying these two, expected strong, lines for Pm-like W (W^{13+}). The fact that these lines do not appear as strong features in the beam-foil spectra should not be taken as a discouraging way. The population mechanisms for excited states in the beam-foil interaction are not expected to be the same as those in a Tokamak plasma. It is evident however that the excitation mechanisms in an Electron Beam Ion Trap (EBIT) are more similar to those in a Tokamak plasma, disregarding the active diagnostic lines for now. Hence we made a search for the Pm-like doublet in the spectra of W using the Berlin EBIT. This led to rather clean spectra compared to the beam-foil case, as we may expect from the cleaner excitation conditions.

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TWO-PHOTON EXCITATION/IONIZATION OF 1S-SHELL OF HIGHLY CHARGED IONS

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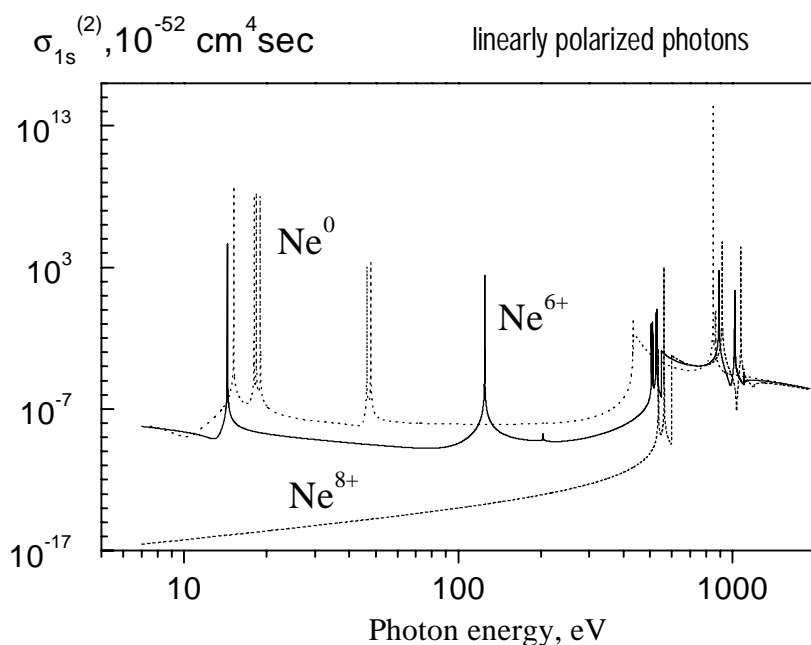
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The cross section of two-photon absorption by neutral many-electron atoms' inner shells are calculated. The case of *Cl* atom [1] and case of *Ne* atom [2] are considered.

The aim of this work is to calculate the cross section of two-photon absorption by an inner shell of highly charged positive ions with inclusion of the relaxation effects and the effect of vacancy stabilization. A simple system with 1S_0 ground state term is chosen as the subject of the study, namely, Ne^{6+} and Ne^{8+} ions. The calculations are fulfilled both for linear and circular polarization of the laser beam.

The calculation results of cross section absolute values and shape of the considered process (excitation/ionization of 1s-shell of Ne^{6+} , Ne^{8+} ions and neon neutral atom by two linearly polarized photons) accounting both the effect of relaxation of the atomic residue in the field of the creating vacancies and the effect of 1s-vacancy stabilization are presented in Figure. Dotted line – for the Ne^0 atom [2]; solid line – for the Ne^{6+} ion; short dashed line – for the Ne^{8+} ion.

The strong dependence of absolute values and shape of the cross section on the ion charge is predicted.



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PHOTOIONIZATION MASS SPECTROMETRY OF PRIMARY PHOTOFRAGMENTS

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Electronically excited atoms and molecules are often formed as reactive intermediates in photon induced fragmentation processes from molecular precursors. They are of considerable interest in the context of atmospheric physics and chemistry as well as astrophysics. Their properties are often unknown, since they are formed in high dilution in the gas phase and they are known to relax rapidly upon collision processes in dense atmospheres. Conventional methods for producing electronically-excited transient species make use of microwave discharges. More suitable is the pulsed laser photolysis of molecular precursors.

A novel experimental approach is presented that allows us to study the photoionization of laser-generated photofragments in the vacuum-ultraviolet (VUV) regime ($E=8-25$ eV) [1]. Photoionization is carried out after formation of excited photofragments by using time-correlated, tunable laser-produced plasma VUV-radiation. A time-of-flight mass spectrometer is used to measure partial ion yields of the primary photoproducts as a function of the VUV-photon energy. Figure 1 shows as a typical example the photoionization cross section of excited atomic oxygen ($O(^1D)$) in the energy regime between 12 eV and 18 eV [2]. $O(^1D)$ is generated as a primary photofragment of ozone (O_3) by primary photolysis at $\lambda=270$ nm. It is found that direct photoionization does not occur in the first (4S ($E>11.65$ eV)) continuum of O^+ , but cation intensity is present in higher continua (2D ($E>14.98$ eV) and 2P ($E>16.67$ eV)). Intense resonances are observed below the 2D -continuum which are due to L/S-forbidden transitions into autoionizing singlet Rydberg states.

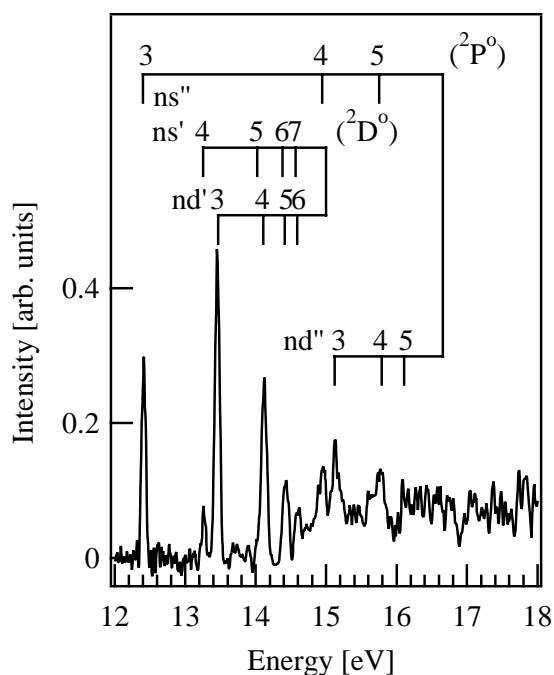


Figure 1: Photoion yield of O^+ from $O(^1D)$ in the VUV-regime. Transitions into autoionizing Rydberg states and their respective convergence limits are indicated.

Results from recent work on the photolysis of atmospheric trace gases, such as chlorine monoxide (ClO), chlorine dioxide (ClO₂), dichlorine peroxide (ClOOC), and nitryl chloride (ClNO₂) [3] is presented, where autoionization and ionization thresholds serve for the selective detection of the quantum states of primary photofragments. Absolute atomic photoionization cross sections allow to derive reliable branching ratios and quantum yields of competing photolysis processes.

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HIGH-RESOLUTION SPECTROSCOPY OF CORE-EXCITED MOLECULAR VAN DER WAALS CLUSTERS

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Resonant core level excitation in the near-edge regime of variable size molecular clusters provides unique information on size effects of matter. High-resolution, state-of-the-art beamlines at high brilliance storage rings allow for the first time investigations on vibrationally resolved inner-shell excitation in free clusters consisting of simple molecules. We report recent results on vibrationally resolved core-to-valence transitions of N_2 ($N\ 1s \rightarrow \pi^*$) and CO ($C\ 1s \rightarrow \pi^*$ and $O\ 1s \rightarrow \pi^*$) and their clusters. The experiments are carried out at the U49/1-SGM-beamline at the storage ring BESSY-II, where partial ion yields of isolated molecules and clusters are measured simultaneously. Small energy shifts that are far below the natural linewidth ($\Delta E \geq 1\text{ meV}$) and changes in intensity between isolated molecules and clusters can be observed.

Small spectral redshifts relative to the isolated molecule, that are of the order of a few meV, as well as changes in line widths and line shape are observed in core-to-valence transitions. These changes are found to depend sensitively on the excited core-edge, corresponding to a site-specific behavior.

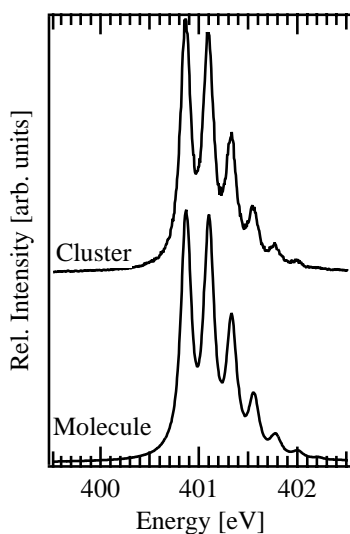


Figure 1: Partial ion yields of molecular and clustered nitrogen in the $N\ 1s \rightarrow \pi^*$ regime. The average cluster size $\langle N \rangle$ is estimated to be ≈ 150 .

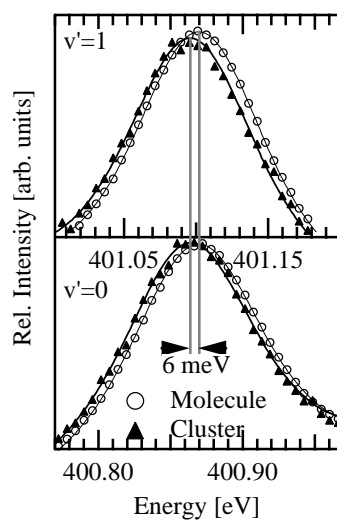


Figure 2: Detailed view on the first two vibrational transitions of the $N\ 1s \rightarrow \pi^*$ -band. Open circles and solid triangles: experimental data points; solid lines: Voigt fit of the experimental data.

Furthermore, the FC-factors of the higher vibrational transitions are reduced in clusters, which is assigned as evidence for slight changes in intramolecular geometry in clustered molecules. The results are discussed in terms of size-dependent changes in electronic and geometric structure upon cluster formation as well as dynamic stabilization of core-excited molecules that are localized in clusters using the quasiatomic approach.

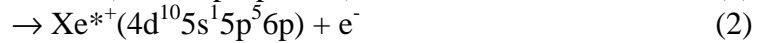
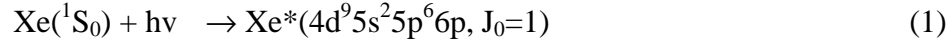
AUGER CASCADE PROCESS OF XE FOLLOWING $4d_{5/2}^{-1}6p$ EXCITATION

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Recent studies [1] on the cascade Auger process following the $2p^{-1}4s$ excitation in Ar showed that angular distributions are very sensitive to relativistic effects. Within the multiconfiguration Dirac-Fock (MCDF) formalism mixing of configurations was also important, signaling the rather strong electron-electron correlation.

In this work, the transition rates and angular distribution of the Xe cascade process



have been studied theoretically and compared with experimental spectra.

The transition rates and the angular distribution parameters for the first and second step Auger transitions have been calculated using the MCDF method. We have also investigated configuration interaction (CI) effects due to the mixing of $4d^{10} 5s^1 5p^5 4s$, $4d^{10} 5p^3 5d^1 6p^1$ and $4d^{10} 5p^3 6p^1 6s^1$ configurations.

The first and second step Auger spectra of Xe were measured with very high photon and electron energy resolution at the I411 undulator beamline at Max-laboratory in Lund, Sweden. In order to determine the angular anisotropies of resonant Auger transitions the rotatable SES-200 electron analyser was set at angles 0° , 54.7° and 90° with respect to the electric vector of the incident light.

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CASCADE DECAY OF INNER-SHELL HOLE STATES OF ATOMIC MAGNESIUM STUDIED BY PHOTOELECTRON-PHOTOION COINCIDENCE SPECTROSCOPY

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The photoelectron-photoion coincidence technique has been shown to be a very versatile method for the investigation of the decay channels of atomic inner-shell hole states. In this technique an initial hole state is identified by a signal of the electron energy analyser which simultaneously serves as a start signal for a time-of-flight measurement for the coincident photoion with respect to its charge state. The ratio of the differently charged photoions then gives information about the decay routes.

For the case of non-cascading transitions the ratio of radiative to non-radiative transitions or the ratio of single to double Auger transitions can be directly related to the corresponding ratios of the differently charged photoions. For cascading transitions, however, additional coincidence measurements are needed. As the first element in the periodic table Magnesium ($1s^2 2s^2 2p^6 3s^2$) shows these cascading transitions.

We investigated the whole cascade of Magnesium by using our photoelectron-photoion coincidence technique on the 1s-, 2s-, and 2p-decay. The new undulator beamline U41-PGM at BESSY II delivered enough flux to realize these measurements on free Magnesium atoms in the whole energy range needed, i.e. at 1400 eV for the 1s- and at 170 eV for the 2s- and 2p- decay.

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PCI EFFECTS IN XENON 4d PHOTOIONIZATION FOLLOWED BY TWO AUGER ELECTRON EJECTION

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We report an investigation of two Auger electrons, one very slow, one fast, which have been detected in coincidence following near threshold 4d-photoionization of the Xe atom. The energy distribution or line shape of the fast Auger electron was measured at photon energies in the threshold region for the inner-shell ionization process where the photoelectron energy varied from near zero to 30 eV. The measurements were made at Super ACO in France¹ and at the Photon Factory in Japan². For analysis we selected two line shapes of the fast electron, associated with a zero-energy electron, which have energies near 3.4 eV and 5.4 eV. These electrons can be the result of Auger decay of both the 4d_{5/2} and 4d_{3/2} holes of the Xe⁺ ion to the ground state of Xe³⁺. All the measured spectra reveal PCI effects that shift and broaden the line shapes, this distortion decreasing with increasing excess photon energy.

There are three possibilities whereby the 4d holes decay ejecting two electrons, one of which has zero kinetic energy: double Auger decay (DA) where two electrons are ejected simultaneously and cascade Auger decay where the two electrons are emitted sequentially the fast electron being the first (CA1) or the second (CA2) emitted. The theoretical description of PCI distortion of the Auger lines is based on the eikonal approach for both the cascade Auger process and the double Auger process³. We have calculated the incoherent contribution of the three processes to the cross section and estimated their role.

Our calculations show quite reasonable agreement of CA2 curves with the experimental data compared to those for DA and CA1. The best agreement with experiment was obtained for a width of the intermediate state, Γ , in the range: 45 meV < Γ < 70 meV. So comparison of the experimental data with the prediction from our calculations clearly demonstrated that the dominant process is CA2 in both 4d_{5/2} and 4d_{3/2} decay.

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OBSERVATION OF TRIPLET DOUBLY EXCITED STATES OF HELIUM BELOW SECOND IONIZATION LIMIT.

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The helium atom is an archetypal three body system ideal for the study of electron correlation. Doubly excited states of helium have been studied extensively and, since these states are imbedded in an ionization continuum, autoionization was, for a long time, considered to be the only appreciable decay channel. So, the ion yield was considered to be a good measurement of the photon absorption cross-section. However recent experiments [1][2] have shown that some aspects of the formation and decay of doubly excited states had been overlooked: this concerns the fluorescence decay of doubly excited states and the role of relativistic effects .

An important experimental advance was made by the detection of the fluorescence products namely UV photons [1] and also metastable atoms [2]. The availability of third generation synchrotron sources with high photon flux and resolution now allows new insight in this domain.

We present here results obtained on the gas phase beam line in Elettra. The states studied are He 2nl' states below the second ionization limit of helium. We have detected both UV photons (2p->1s) and metastable atoms resulting from radiative decay of helium doubly excited states. The very high sensitivity of metastable detection has allowed the first direct observation of LS forbidden doubly excited triplet states [3]-

Two new series are clearly observed: the 2pnd ³D₁^o and the (sp, 2n-) ³P^o. Excitation of these states is possible due to spin orbit interaction of the 'inner' 2p electron which can overcome the Coulomb electron-electron interaction for high n values. A simple first order perturbation model accounts for the excitation of these states with essentially triplet character via their mixing with (sp, 2n+) ¹P^o optically allowed states. They decay essentially to the metastable 2³S state of He and this process is responsible for the intense metastable signal below threshold.

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HIGH RESOLUTION AUGER SPECTROSCOPY: APPLICATION to the COSTER KRONIG DECAY of the Ar 2s HOLE

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An Auger spectrum gives clues to both the dynamics of the associated inner shell hole decay and to the spectroscopy of the final doubly charged ionic state. However, this information is blurred by two factors: (1) raw Auger spectra contain the contributions associated with different initial hole states, (2) the resolution of the final state is limited by the lifetime of the initial inner shell hole. In order to overcome these two limitations, we are developing a technique based on photoionisation and the use of synchrotron radiation. It consists simply in measuring the Auger spectrum in coincidence with the photoelectron that defines the initial hole. It is clear that only the Auger spectrum associated with this well defined hole will be recorded. It can also be shown, by simple energy conservation arguments, that the limitation associated with the hole lifetime is removed [1]. This situation is referred to as the "sub-lifetime regime" [2].

Our experiment [3] uses a high luminosity threshold electron spectrometer, dedicated to the detection of the photoelectron, and for the Auger electron, a hemispherical electrostatic analyzer, equipped with a two dimension position sensitive detector. Measurements on Argon were made on the BL16 beam line at the Photon Factory, Japan, in January 2001.

We will present at the conference new results on Argon 2s Coster-Kronig decay. The 2s hole is known for its extremely short lifetime τ , that causes a broadening of $1/\tau = 2.25$ eV of the Auger spectrum. This obscures the intensities and positions associated with the Ar^{++} state thus created, whether measured in electron [4] or photon [5] impact. In a previous experiment, with a 600 meV resolution [1], we revealed structure hidden in the non-coincident Ar $L_1L_{2,3}M_{2,3}$ spectrum. Our new measurement reached a better resolution of 500 meV for these $\text{Ar}^{++} 2p^{-1}3p^{-1}$ states. Furthermore, they located the $\text{Ar}^{++} 2p^{-1}3s^{-1}$ states and revealed the satellite lines, associated to $\text{Ar}^{++} 2p^{-1}3p^{-2}nl$ configurations, that have recently been predicted [5].

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ANGULAR DISTRIBUTION IN RESONANT AUGER SPECTRA OF XENON EXCITED BELOW THE $3d_{5/2}$ IONIZATION THRESHOLD

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So far the study of the Xe $3d_{5/2}^{-1}np$ ($n = 6,7$) core hole resonant states (Figure 1) has been modest due to very small excitation cross-sections and relatively high binding energies. The strong development of both the synchrotron radiation sources and the analyzers has, however, made it possible to study such weak resonant states. The angle-resolved Xe $3d_{5/2}^{-1}np \rightarrow 4d^2np$ resonant Auger spectra (Figure 2) [1] were measured at the Gas Phase Photoemission beamline of Elettra storage ring in Trieste, Italy, using an end station equipped with an array of hemispherical electron energy analyzers. Comparison with corresponding normal Auger measurements [2] reveals the role of the resonantly excited electron and its effects on energy, intensity and angular distributions. Furthermore, the angle-resolved measurements confirmed experimentally the theoretical gross spectator model [3,4].

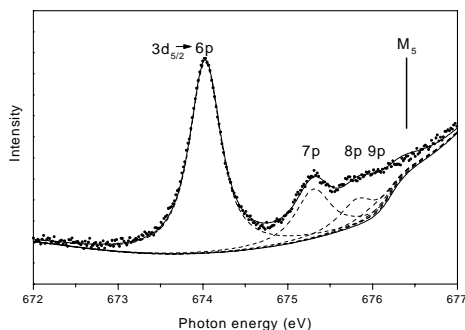


Figure 1. M_5 pre-edge Rydberg excitations in Xe.

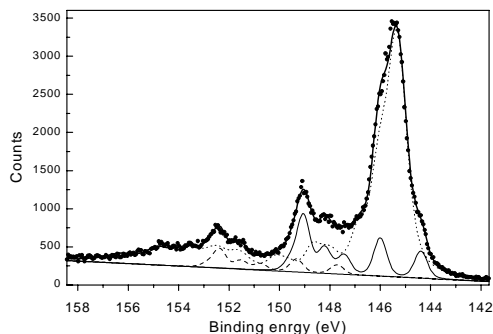


Figure 2. The electron spectrum of Xe at the $3d_{5/2}^{-1}6p$ excitation.

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High resolution Auger spectroscopy of free barium atoms

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Atomic barium is an excellent system to study electron-electron correlations, due to the strong correlations of the valence electrons in the 4d excited state. This is caused by the collapse of the 5d wavefunction resulting in a near degeneracy of the 6s, 6p, 5d and 4f electrons. High resolution experimental Auger electron spectra subsequent to a 4d photoionization have been measured at the AMO undulator beamline 10.0.1 of the Advanced Light Source (ALS) synchrotron radiation facility at Lawrence Berkeley National Laboratory using a Scienta SES200 high resolution electron spectrometer [1]. The present measurements were all performed at an emission angle of 54.7° with respect to the electric field vector, in a plane perpendicular to the propagation direction of the beam of linearly polarized photons. The analyzer was operated at the constant pass energy of 40 eV with an electron energy resolution of 40-50 meV. The Auger spectra have been measured at a photon energy of 131 eV to avoid any overlap between Auger and photo lines.

In recent studies of the 5p and 4d photoionization of atomic barium, the experimental photoelectron spectra have been described theoretically in great detail by a configuration interaction (CI) approach using Hartree-Fock wavefunctions as a zero order approximation [2,3]. Since the agreement with the measurements were excellent, we decided to perform similar calculations to analyze the NOO Auger electron spectra.

The overall agreement between the measured and calculated Auger spectra is very good. However, an assignment is possible only for a very limited number of lines, because the Auger spectra consist of thousands of lines. For this reason we have calculated the term dependent Auger spectra, i.e. the spectra which originate from the different initial hole states corresponding to the different lines of the satellite-rich 4d photoelectron spectrum. We found striking differences between the Auger decay of the final states of the photoionization process, which can be attributed to the strong electron-electron correlations. These results enable us to assign several more Auger lines to Ba^{2+} states.

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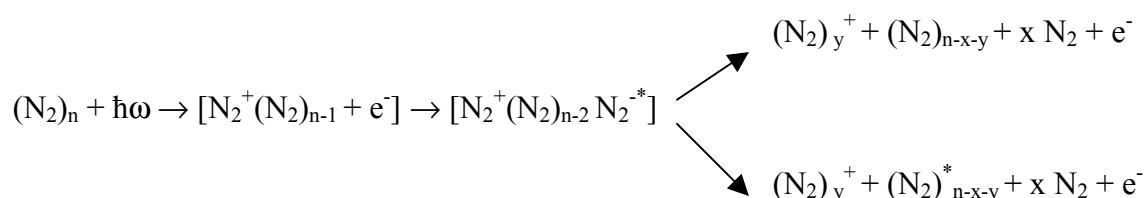
INNER-SHELL EXCITATION AS A PROBE OF INTERMOLECULAR INTERACTIONS

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Perspectives on inner-shell excitation as a probe of intermolecular interactions are presented. These are provided by the recent experimental progress in experimental high resolution studies on Van der Waals clusters [1,2] and the development of the quasi-atomic approach [3,4] that allows to describe core-to-valence transitions, such as $1s \rightarrow 1\pi_g^*$ (π^*) and $1s \rightarrow \sigma_u^*$ (σ^*), in nitrogen and carbon monoxide. The concept of dynamic core-hole localization allows us to examine site-selectively changes in electronic and atomic structures of Van der Waals molecules, which includes a fast probe of intramolecular and intermolecular dynamics. Photoprocesses, such as



are considered which influence the $1s$ photoabsorption and photoionization cross sections at intermolecular distances that are close to the intermolecular Van der Waals distance in weakly bound species. Essential changes in electron-optical properties and intermolecular dynamics of molecular nitrogen are revealed at the σ_u^* -shape resonance and near the $1s$ -ionization threshold. Recent high resolution studies indicate that there are distinct changes in vibrational fine structure of the low-lying $1\pi_g^*$ (π^*)-resonance upon the transition from the isolated molecule to clusters [1,2]. These changes can be due to: (i) freezing of molecular rotations, (ii) the occurrence of intermolecular vibrations (soft modes), and (iii) dynamic stabilization of the core-excited molecule, resulting in a slight redshift of the vibrationally resolved core-to-valence transitions, which is of the order of a few meV [1]. It is shown that the intermolecular vibrations lead to phonon-like broadening and dynamic stabilization converts to a polaron-like shift, when the number of molecules in a cluster reaches infinity. Dynamic stabilization is primarily due to changes in intermolecular interactions that are induced by the inner-shell excitation process. Model studies on N_2 that is confined within an endohedral environment (e. g. within a fullerene system) are also presented in order to illustrate general importance of dynamic stabilization.

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LARGE NONDIPOLE EFFECTS IN THE CORE-LEVEL THRESHOLD REGIONS OF SMALL MOLECULES

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The electric-dipole or uniform-electric-field approximation has long served as a basis for understanding many aspects of the interactions between radiation and matter. Deviations from the dipole approximation (DA) for atomic targets can be attributed to the variation in phase of the incident radiation over the spatial dimensions of the absorbing charge distributions, which incorporates higher (electric quadrupole, magnetic dipole,...) terms into the radiation-matter interaction. Accordingly, significant departures from DA are commonly thought to occur only at wavelengths comparable to or smaller than the spatial dimensions of the absorbing electronic orbitals, an expectation born out by recent experimental photoionization studies on rare gas atoms performed at sufficiently high photon energies [1]. Somewhat surprisingly, however, other recent experiments and theoretical calculations have demonstrated atoms also may exhibit significant nondipole effects which are somewhat beyond the usual dipole expectations also at longer incident photon wavelengths [2]. Recent experimental results on N₂ [3] with a detailed theoretical analysis of the contributions of first-order nondipole terms to the interactions between radiation and matter attributes the observed behaviors about 60 eV above threshold to the presence of strongly anisotropic bond-length-dependent photoionization amplitudes, and suggests that those results may be indicative of a potentially universal behavior in molecular photoionization more generally.

Here we report experimental observations of significant deviations from the DA in the angular distributions of K-shell electrons photoemitted from gas-phase CO and N₂. In contrast to the situation for atomic targets [1,2] and the previous observations in N₂ [3], large deviations from the DA are found at suprisingly low incident photon energies just a few eV above the core-level ionization thresholds in CO and N₂. The measurements were performed at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory on undulator beamline 8.0. The ALS, operated in two-bunch mode, providing a photon pulse every 328 ns, allowing photoelectron detection using the time-of-flight technique which is described elsewhere [4].

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PHOTOABSORPTION CROSS SECTIONS OF PLANETARY MOLECULES IN THE VUV RANGE

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Absolute photoabsorption cross sections of several planetary molecules and their isotopomers have been measured in the VUV range. For this purpose we used a dual beam absorption set-up to normalize the intensity fluctuation of the light source, as shown in Figure 1. The light of VUV was the synchrotron radiation dispersed with beam line located at the Synchrotron Radiation Research Center in Taiwan. Absorption spectra of samples were recorded at various pressures. At each wavelength absorbance ($=\ln(I_0/I)$) determined at 5 to 20 pressures was plotted against number densities and fitted with least-squares method to a line to yield absorption cross section according to the Beer's law.

Photoabsorption cross sections of H₂O, HDO, D₂O, CH₄, CH₃D, C₂H₆, C₂H₅D, HCl, DCl, CH₃OH, CH₃OD, CD₃OH, and CD₃OD have been measured. Results combined with the information of isotopic fractionation of planetary molecules can be applied to the understanding of atmosphere and evolution of planets. For example, the major implication of H₂O and HDO data is on the evolution of Martian water, which must have lost at least a 50-m global layer of water.

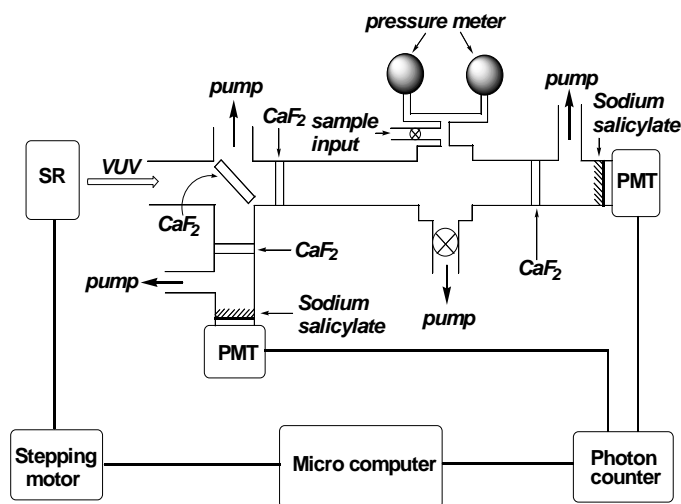


Figure 1: Schematics of the dual-beam photoabsorption experiment.

SYMMETRY-RESOLVED VIBRATIONAL SPECTROSCOPY FOR THE $C1s^{-1}$ EXCITED RENNER-PAIR STATES IN CO_2

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Carbon dioxide (CO_2) is a linear molecule in the ground state. When the Carbon $1s$ core electron is excited to the lowest unoccupied molecular orbital $2\pi_u$, the doubly degenerate $C 1s^{-1} 2\pi_u$ states split into Renner-Teller pair states. The lower-energy state has a bent stable geometry while the other has a linear stable geometry. The bent state has a π electron whose orbital lies in the bending plane of the molecule (in-plane A_1 in C_{2v}) while the linear state has the out-of-plane π electron (out-of-plane B_1 in C_{2v}). We present the vibrationally-resolved spectra for symmetry-resolved A_1 and B_2 excitations.

Angle-resolved ion-yield spectra for the $C 1s \rightarrow 2\pi_u$ resonance were first obtained by Adachi *et al.* [1] at the Photon Factory. They suggested that the shift of the peak positions for the energetic-ion-yield spectra recorded in the direction parallel and perpendicular to the polarization vector of the incident light is ascribed to the Renner-Teller splitting but they could not resolve any vibrational structures. Total ion yield spectrum was measured by Kukk *et al.* [2] at the ALS at higher resolution. They observed a vibrational progression with spacing of 151 meV and assigned it to the symmetric stretch mode (ν_1) of the linear B_1 state.

We have carried out angle-resolved ion-yield spectroscopy on the c branch of the beamline 27SU at SPring-8 in Japan. This beamline provides linearly polarized monochromatic soft X-ray with the photon band pass of < 30 meV in the $C 1s$ excitation region. Energetic ion yield spectra $I(0)$ and $I(90)$ were recorded using two identical high-pass (> 6 eV) ion detectors mounted in the direction parallel and perpendicular to the polarization vector of the incident light. The total ion yield (TIY) spectrum was also measured at the same time. In the TIY spectrum, we could clearly observe two vibrational progressions with the mean vibrational spacing of 140(10) meV. Note that the energetic ion yield spectrum $I(0)$ directly reflects the excitation spectrum to the A_1 state. Combining the present yield spectra $I(0)$ and $I(90)$ with the excitation ratios to the A_1 and B_1 states measured by means of the triple-ion-coincidence momentum imaging method [3], we have obtained symmetry-resolved absorption spectra for the A_1 and B_1 excitations. One vibrational progression with the mean vibrational spacing of 140(10) meV is recognized in each spectrum. These progressions are assigned to the symmetric stretching modes in the core-excited A_1 and B_1 states.

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MIRRORING DOUBLY EXCITED RESONANCES IN RARE GASES

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The electronic structure of atoms is still a generally unsolved problem due to many-body interactions. One manifestation of such interactions is the resonant excitation of two electrons to previously unfilled orbitals, following absorption of a single photon. While this process has received much successful theoretical attention for atoms such as helium and lithium, the results for more complex atoms have not been so successful, due in part to the increasing importance of relativistic effects. The significance of these and other effects is difficult to assess in general. However, with the aid of experimental results from third generation light sources, indications can be found to guide theoretical efforts.

One example is the study of the autoionization of doubly excited resonances in argon. The highest resolution data for resonant processes has commonly been obtained using total cross-section measurements. However, there is a class of resonances, whose contribution to the total cross-section can be zero and may only be observed in measurements of partial cross-sections. They are characterised by equal and opposite resonant contributions to the individual partial cross sections and are termed *mirroring resonances*[1].

Recent measurements[2,3] below the 3s ionization threshold in argon represent an elegant example of the mirroring phenomenon. Previously, the photoionization spectrum of argon[4] in this region showed the $3s^{-1}np(^1P_1)$ Rydberg series, and two low-lying, doubly-excited resonances, $3s^23p^44s(^2P_{1/2,3/2})4p(^1P_1)$. However, partial cross-section measurements have revealed two resonant states between the $n = 7$ and 8 singly excited states. These resonances have profiles which mirror each other in each of the two final channels and so when added, cancel such that there is no discernible presence in the summed spectrum. Consequently, even higher resolution total cross-section spectra may not be able to see such spectral features where present.

The requirements for such perfect mirroring give, in the current case, an indication of the level of spin-orbit effects in this particular spectral region. The new resonances have been determined to be LS-forbidden triplet doubly-excited states[2]. Therefore, if spin-orbit effects are not accurately modeled theoretically, the resulting cancellation will not be so complete. These types of measurements then provide a sensitive testing ground for future calculations which attempt to characterise spin-orbit effects.

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High resolution investigation of the Ne^+ satellite states near threshold

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The ejection of one electron and the simultaneous excitation of another one occur in several cases of atomic photoionisation. The study of these satellite transitions gives detailed information on the dynamics of many-electron interactions. The study of the $\text{Ne}^+ 2p^{-2}n\ell$ satellite states have been performed at Elettra combining the high efficiency of a threshold photoelectron analyser and the high resolution of the Gas Phase beamline, while the study of the $\text{Ne}^+ 2s^{-1}2p^{-1}n\ell$ satellites has been done at the TGM beamline of the Daresbury SRS. The two measurements together represent the most extensive investigation of the Ne^+ satellites, that spans from below the $\text{Ne}^+ 2s^{-1}$ threshold (48.48 eV) up to the $\text{Ne}^{2+} 2s^{-1}2p^{-1} ({}^1\text{P})$ threshold (≈ 98.44 eV). While the region of the $2p^{-2}n\ell$ states has been previously investigated, although at lower energy resolution (1), no data near threshold exist for the region of the $2s^{-1}2p^{-1} n\ell$ states.

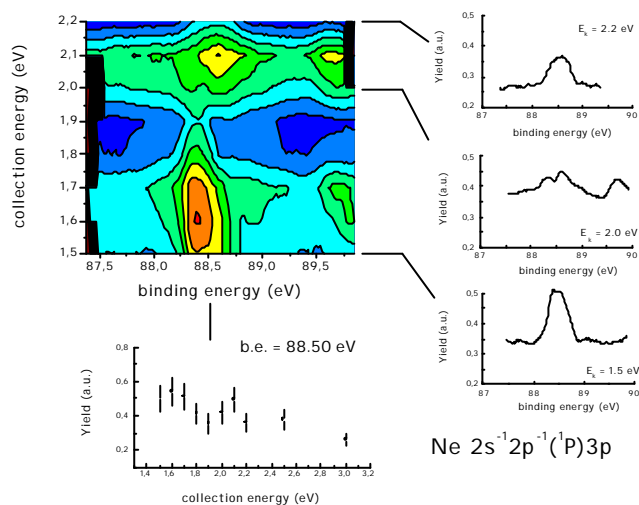


Figure 1. PES of the $\text{Ne}^+ 2s^{-1}2p^{-1}({}^3\text{P})3p$ state at various collection energies E_k .

In addition several spectra of the $\text{Ne}^+ 2s^{-1}2p^{-1}({}^1\text{P})3p$ ion state have been measured at different kinetic energies of the photoelectron. The results, shown in fig.1, display an anomalous behaviour of the photoelectron peak while varying the kinetic energy of the photoelectron near 2 eV. This has been interpreted as an indication of an interference effect between two paths leading to the $\text{Ne}^{2+}(2p^{-2}{}^3\text{P})$ continuum.

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ELECTRONIC STRUCTURE AND ENERGY RELAXATION OF DOPED RARE GAS CLUSTERS WITH A SHELL-LIKE STRUCTURE

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The electronic structure and dynamics of clusters has attracted considerably interest for many years since it gives new insight in the properties of condensed matter. Investigations on doped species offer the opportunity to get information about the host cluster and the impurity, because the excitation is usually localised on the impurity atom. In this contribution, we report on energy dissipation processes in Ar_M clusters ($M < 80$) covered with a shell of Kr atoms (up to 30 atoms) and embedded in large Ne_N clusters ($N = 3500$). The $\text{Ar}_M\text{Kr}_K\text{Ne}_N$ complex is studied with energy-resolved fluorescence excitation spectroscopy.

Doped clusters are prepared in a supersonic expansion and subsequent pick up of atoms from two cross-jets. After excitation with monochromatic synchrotron radiation (11-22.5 eV) the emitted fluorescence light is detected by two photomultipliers (sensitivities: 2-6 and 4-11 eV). For spectrally resolved measurements in the visible and near-infrared spectral range a monochromator with a CCD camera is used. The absorption of clusters is monitored by fluorescence excitation. In the energy range of the Ar cluster absorption (11-13 eV) the intensity ratios of bands differ considerably from those of free clusters due to the influence of the shell atoms. The surface states disappear and a new absorption band occurs, which we interpret as Ar-Ne-interface excitations. The dependence of the transition energies on the size of the embedded Ar clusters can be explained using the Frenkel-exciton model. Dipole transition moments could be derived from the energy shifts. They are in good agreement with those of the corresponding molecular Ar_2 transitions.

After excitation into the Ne $11'$ -exciton the fluorescence spectrum of Ar clusters embedded inside Ne clusters consists of sharp lines which are due to free atomic Ar transitions ($4p \rightarrow 4s$). Electronically excited Ar atoms move through the Ne cluster, desorb and emit in the vacuum. By coating the Ar cluster with Kr atoms, the Ar lines disappear and $5p \rightarrow 5s$ transitions of Kr become dominant. Additionally, new bands occur, which we interpret as Ar transitions of perturbed atomic $4p$ -states inside Ne clusters. We suggest a simple kinematic model to describe the movement of excited Ar atoms inside Ne clusters.

INHERENT LIFETIME WIDTHS OF AR $2p^{-1}$, KR $3d^{-1}$, XE $3d^{-1}$ AND XE $4d^{-1}$ STATES

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The lifetime is one of the most fundamental factors characterizing a core-ionized or a core-excited state. Yet core-hole lifetimes of even rare-gas atoms are rather poorly known. Perhaps the most straightforward method to determine the lifetime of a singly ionized species is photoelectron spectroscopy. The lineshape of a core photoelectron line is given by the convolution of the Lorentzian lifetime broadening, Doppler broadening and the instrumental broadening. The latter is further composed of the photon energy and kinetic energy contributions, and is often approximated to have a Gaussian shape. Recent development in synchrotron radiation sources and electron analyzers has greatly diminished the instrumental broadenings, making it possible to determine the lifetime widths more accurately.

The measurements were performed on the I411 [1] undulator beamline at the MAX II storage ring at Lund, Sweden. Synchrotron radiation was monochromatized with a modified SX-700 plane grating monochromator. The photon energy resolution of the beamline is competitive in the photon energy range 55–300 eV and reasonably good up to 900 eV. The ejected electrons were energy analyzed with a high-resolution Scienta SES-200 electron spectrometer. The kinetic energy resolution of the analyzer was determined by recording the Kr 4p photoelectron lines that have essentially zero lifetime broadening. The Ar 2p, Kr 3d, Xe 3d, and Xe 4d photoelectron spectra were measured at several photon energies, keeping as many experimental parameters the same as possible as in the Kr 4p calibration measurements.

The inherent lifetime widths of the Ar $2p^{-1}$, Kr $3d^{-1}$, Xe $3d^{-1}$, and Xe $4d^{-1}$ states were determined with higher experimental resolution than before. The results are compared with the previous determinations and also with the lifetime broadenings obtained for the corresponding core-excited states using photoabsorption or electron energy loss spectroscopies.

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ION-PAIR FORMATION FROM DOUBLY EXCITED RYDBERG STATES IN NO, O₂, AND CO

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Ion-pair production is an important method for the investigation of highly excited states of neutral molecules. In particular doubly excited Rydberg states, lying between the single and double ionization thresholds provide fundamental information on electron correlation [1].

We have measured negative ion yield curves using synchrotron radiation in the energy range 18-55eV in O₂, CO and NO gases. A large number of states are observed as resonances over the entire energy range. Figure 1 displays the O⁻ yield in NO in the region of the lowest thermochemical threshold and shows that pair production proceeds via direct and predissociating Rydberg states. The results in figure 2 illustrate for the first time the existence of a number of quasibound excited electronic states of NO around the double ionization threshold and the binding energy of the 1σ molecular orbitals. Further work is needed to uniquely identify these resonances and their decay channels.

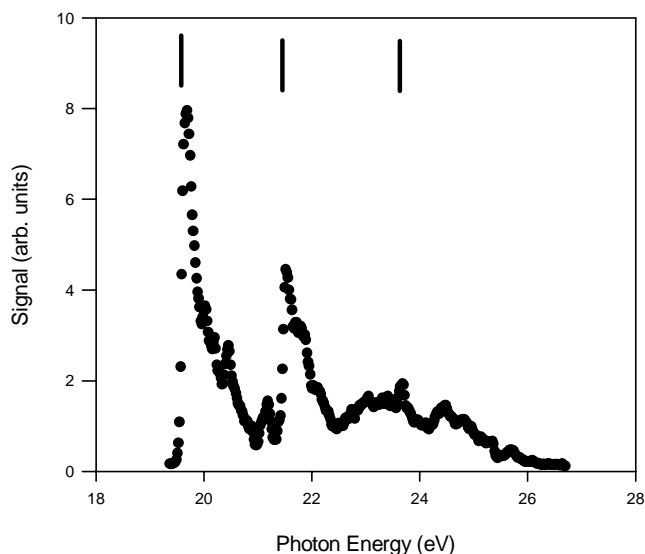


Figure 1: O⁻ formation from NO in the region of the thermochemical threshold. Lines indicate N⁺(³P), N⁺(¹D) and N⁺(¹S) ions.

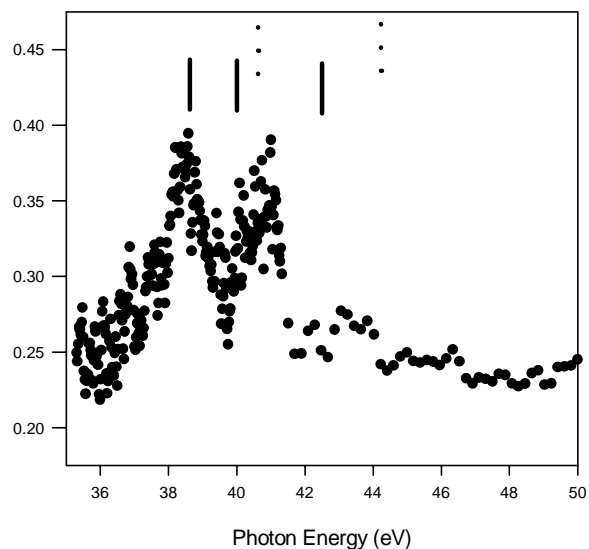


Figure 2: O⁻ formation from NO in the region of known NO⁺⁺ states (solid lines) and the binding energies of the 1σ molecular orbitals (dotted lines)

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PHOTOIONISATION OF ETHANE IN THE VUV

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The study of the ionization and fragmentation processes in ethane C_2H_6 is particularly important since this molecule has been prominently and quite successfully treated in theoretical calculations based on the statistical quasi-equilibrium theory of mass spectra QET [1,2].

We have obtained, using synchrotron radiation within the energy range 11-35eV, both positive and negative ion yield curves in C_2H_6 with better resolution and counting statistics than in all previous work. As can be seen in the ion breakdown diagram (figure 1), the general features are indeed in accord with QET, each successive fragment ion rising from threshold to a long flat plateau. However in several cases, see for example $C_2H_4^+$, we also see significant structure indicating that autoionization and predissociation compete effectively with the statistical energy randomization involving fast coupling between the vibrational modes. Figure 2 shows the negative photoion yield curve of H^- formation in C_2H_6 along with ionization thresholds obtained from photoelectron spectra. Many of the main features correlate with and appear just below these thresholds clearly indicating that superexcited Rydberg states are involved. However additional features, probably due to previously unknown states, are also apparent.

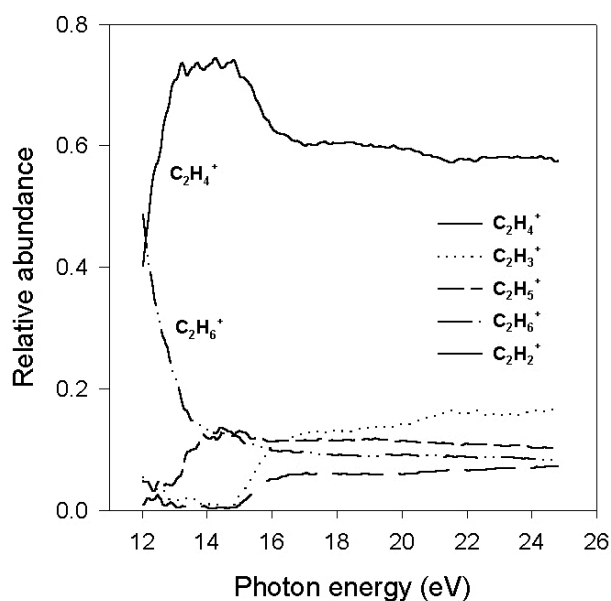


Figure 1: Positive ion breakdown curves from the photoionization of ethane

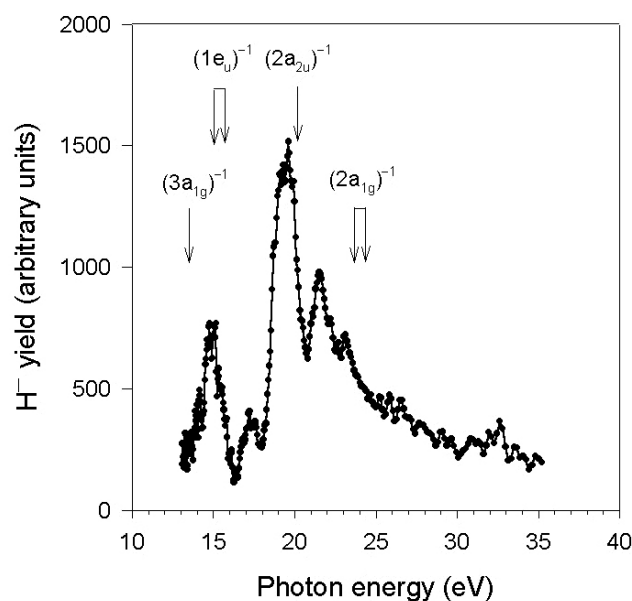


Figure 2: H^- formation in C_2H_6 . The lines indicate known ionization thresholds.

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PROBING ELECTRON ESCAPE DEPTH FOR FREE CLUSTERS

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The variety of processes taking place after X-ray irradiation in solid noble gases has been studied extensively by photoemission, absorption and Auger spectroscopy in bulk and adsorbed multilayers by many authors. Free clusters were always much more difficult for investigation - primarily since the “sample” density was insufficient for most of the X-ray sources [1]. Free clusters however are almost an ideal object for getting the information about the interaction of atoms at the scale of still countable but already quite large amount of participants. For comparison the study of multilayers always has to deal with the influence of the substrate. Thus one of the most puzzling and fascinating things at this nanoscale - the interplay of surface and bulk properties – is obscured by the interface-determined phenomena.

The experiments reported here were performed using the high resolution soft X-ray beam line I411 at the 3rd generation synchrotron radiation facility MAX-II. It allowed obtaining sufficient electron signal from argon and xenon clusters in photoemission studies of the core-level ionisation processes. In the argon 2p and xenon 4d core-level photoemission spectra the resolution was enough to unambiguously separate the contribution of the atoms located on the cluster surface and in the bulk of the clusters. These measurements were performed at different excitation energies covering the range of 200 eV above the ionisation threshold for argon and 100 eV for xenon. It was demonstrated that bulk or surface aspects of the cluster electronic and geometric structure can be emphasized by using different photon energies. From the ratio between the “surface” atom signal to the “bulk” atom signal the efficient electron escape depth was estimated for different electron kinetic energies. These results as well as absorption, normal and resonant Auger studies will be presented in detail.

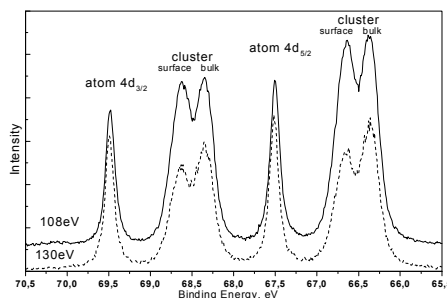


Figure 1: Xe 4d Photoemission spectra for 108eV(solid) and 130eV (dashed). Atomic, cluster bulk and cluster surface signals are indicated.

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Selective fragmentation of valence and core electron excited CD₄ and SF₆ molecules

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Electron-ion coincidence measurements with energy resolved electrons are a powerful tool in studies of molecular fragmentation processes. By analyzing electron kinetic energy only fragmentations from a specific doorway state are monitored while the remaining reactions are discriminated [1]. Presently, we have applied this technique in measurements of coincidence spectra of the CD₄ and SF₆ molecules following valence and core electron excitation. Our experiment has been implemented using an electron-ion coincidence spectrometer. It comprises a 125 mm electron spectrometer and 110 mm time-of-flight mounted collinearly. An inbuilt gas cell provides a target pressure 10-100 times above the chamber pressure. The measurements are performed at the magic angle with respect the synchrotron light polarization's direction.

Our results show that the CD₄⁺ molecule in the 1t₂⁻¹ state is stable or fragments into CD₃⁺ + D only. None of these reactions occur from the 2a₁⁻¹ state for which the D⁺, CD⁺ and CD₂⁺ fragments were observed only. CI computations reveal that the CD₄⁺ fragments into CD₃⁺ + D in a process in which the initially excited ²B₁ state of the C_{2v} geometry undergoes the transition to the state in the C_{3v} geometry which instantaneously fragments to CD₃⁺ + D. Dissociations from the 2a₁⁻¹ state are governed by the 2 ²A₁ states in C_{2v} and C_{3v} geometries. Molecular fragmentation is also studied following core excitations of the C 1s electrons in CD₄. Autoionization of the excited state to the 1t₂⁻¹ state significantly alters the CD₄⁺/CD₃⁺ fragment ratio, which is the first demonstration of a correlation between nuclear motion and molecular dissociation in the CD₄ molecule. In addition, strong spectator Auger transitions that create double-hole ionic states result in a drastically different fragmentation pattern. Molecular fragments D⁺, C⁺, CD⁺ and CD₂⁺ are detected in coincidence with the Auger electrons, indicating a more complete breakdown of the molecule. Our results of the coincidence measurements on SF₆ show that the SF₆⁺ molecule in the 1t_{1g}⁻¹ state is unstable and fully dissociates into the SF₅⁺ + F channel. Also the SF₆⁺ ions in the 4t_{1u}⁻¹ state are unstable and fragments to SF₃⁺ + 3F in full agreement with predictions of Hitchcock et al [2]. Also the mass spectra acquired in coincidence with the 5t_{1u}, 3e_g, 1t_{2u}, 1t_{2g}, and 5a_{1g} electrons reveal strong selectivity in dissociation from these states. This selectivity reflects the bonding properties of the potential surfaces involved in the studied processes.

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”Novel decay processes in core-excited diatomic molecules”

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With the availability of third-generation synchrotron light sources in the soft X-ray regime in combination with high-resolution photoelectron spectrometers, the investigation of very weak processes, often hitherto not possible at all to study, has become feasible. The first example is the N1s $\rightarrow \pi^*$ resonant Auger decay to the B final state in N₂⁺ [Pia00] which demonstrates that a classification of decaying core-hole processes into ”spectators” (2h-1e final state) and ”participators” (1h final state) is too rough in some cases. Other examples are the observation of ”atomic holes” in ultrafast dissociation of core-excited molecules, as recently shown for the decay of the 2p $\rightarrow 6\sigma^*$ core-excited state to the 4 σ^{-1} final state in HCl [Fei00], and the spin selectivity in the vibrational progression of the X-participator decay following the same resonant excitation which revealed a novel type of propensity mechanism [Fin01]. Furthermore, the resonant Auger decay following C1s $\rightarrow \pi^*$ excitation in CO was reinvestigated at high resolution, demonstrating that one can investigate the decay properties of higher vibrational levels than only $v' = 0, 1, 2$, even if these higher vibrational states are not ”visible” in a total ion or total electron yield absorption spectrum [Fei01].

The experimental spectra have been recorded at the undulator beam line I411 [Bäss00], MAX-II, Lund, Sweden, equipped with a modified Zeiss SX 700 monochromator and with a high resolution Scienta SES 200 electron spectrometer. High photon flux combined with state-of-the-art electron energy resolution allowed us to investigate these remarkable decay processes in detail for the first time.

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Observation of quantum oscillations in the C_{70} photoemission partial cross sections up to 200 eV

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Fullerenes, in particular C_{60} and C_{70} , are a very specific form of matter causing unexpected behavior even in such matured fields as photoelectron emission. In recent years it has been shown that the partial photoemission cross sections of the two outermost valence shells of C_{60} show strong oscillations [1-3] due to the potential in which the corresponding electrons are bound. The frequency of the oscillation is related to the average radius of the fullerene molecule, which is for the case of C_{60} the bucky ball radius. In the case of C_{70} which has a more egg like shape the average radius of the rotating molecule should cause the oscillating behavior. Former measurements of C_{70} [4] were not performed at sufficiently close energy intervals in order to prove this assumption. Therefore, a new photoemission experiment of C_{70} was performed at the beamline BW III of HASYLAB and the new MBI-Beamline at BESSY II.

Figure 1 shows ratio of the cross sections of the outermost C_{70} photolines between 40 and 190 eV. The solid line is the result of a fit of the data by an exponentially decaying sine function. The result of this fit gives the mean radius R of the rotating C_{70} molecule. The value is in good agreement with what one would expect from averaging over all three axis of the ellipsoidally shaped fullerene. This corroborates the simple quantum oscillation model used to explain the partial cross section oscillation in fullerenes. The next step of a more sophisticated model would be to look for quantum beats in the oscillations as a signature of the thickness of the real shell like potential in which the electrons are bound [5,6]. Our data are still not taken in fine enough steps as well as limited to too low photon energies in order to draw a conclusion in this direction. This new measurement, however, is a very solid verification of the basic oscillation predicted by the quantum oscillation model for the case of C_{70} .

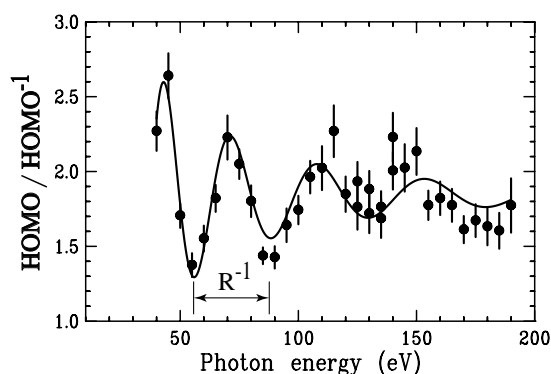


Figure 1: Oscillation in the ratio of the cross sections of the outermost C_{70} photolines.

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CIRCULAR DICHROISM IN THE VALENCE-PHOTOIONIZATION OF FREE NO MOLECULES

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We have measured NO 4σ inner valence photoelectron angular distributions in the molecular frame. Using circularly polarized light of two different helicities we were able to derive the circular dichroism in the angular distribution (CDAD) of the photoelectrons [1]. The CDAD describes the difference between the angular distributions for the two different light helicities. While the angular distributions have to be described by a rather big number of matrix elements and phase shifts, the CDAD is a function of only a few terms containing information on the relative phase shift between the outgoing σ and π continuum waves and the partial wave composition. We observed a remarkable f-wave contribution in the outgoing photoelectron wave which can be explained by the influence of the shape resonance being observed previously in the relevant photon energy region [2,3].

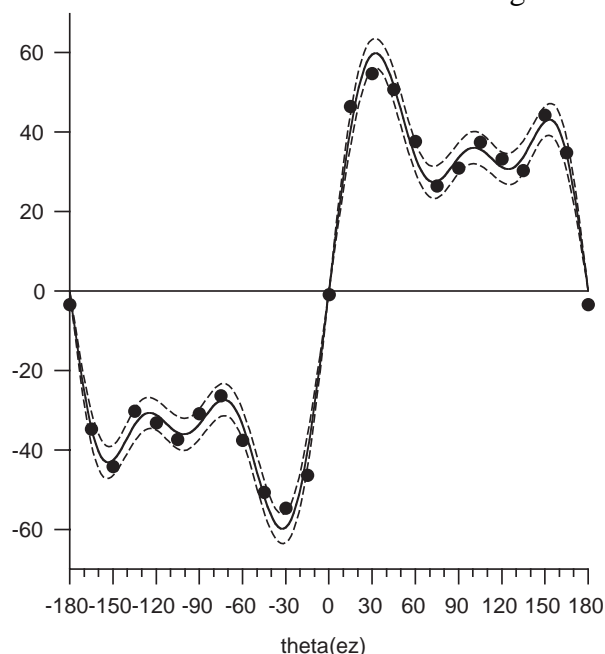


Figure 1: Circular dichroism in the angular distribution (CDAD) of photoelectrons emitted by free NO molecules.

The CDAD describes the difference between the angular distributions for the two different light helicities. While the angular distributions have to be described by a rather big number of matrix elements and phase shifts, the CDAD is a function of only a few terms containing information on the relative phase shift between the outgoing σ and π continuum waves and the partial wave composition. We observed a remarkable f-wave contribution in the outgoing photoelectron wave which can be explained by the influence of the shape resonance being observed previously in the relevant photon energy region [2,3].

The CDAD has previously been measured for molecules adsorbed on surfaces [4]. To our knowledge this is the first time that it has been observed on free fixed-in-space molecules. The target molecules were not statically oriented before the photoionization took place, rather the molecular orientation was derived at the instant of photoionization by measuring the vector correlation between the photoelectrons and the molecular ionic fragments.

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AUGER ELECTRON - ION COINCIDENCE SPECTROSCOPY OF CORE IONISED CARBON DIOXIDE

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The Auger electron - ion double coincidence technique was pioneered by Eberhardt *et al* [1] and extended to a triple coincidence technique correlating Auger electrons with ion pairs by Hanson *et al* [2] and Alkemper *et al* [3]. We will present recent data exploiting both the double and triple Auger electron coincidence techniques with carbon dioxide exploring ion percentage yields and fragmentation dynamics.

As an example, Figure 1 shows the variation of the fragmentation pattern of C 1s ionised CO₂ molecules as a function of Auger electron energy. It is firstly noticeable that the degree of fragmentation decreases with increased Auger energy, as observed by Alkemper *et al* [3] in the case of S 2p ionised CS₂. Such a result may be understood by noting that a high energy Auger electron will leave the final doubly charged molecule in a low lying state, and vice-versa for low energy Auger electrons.

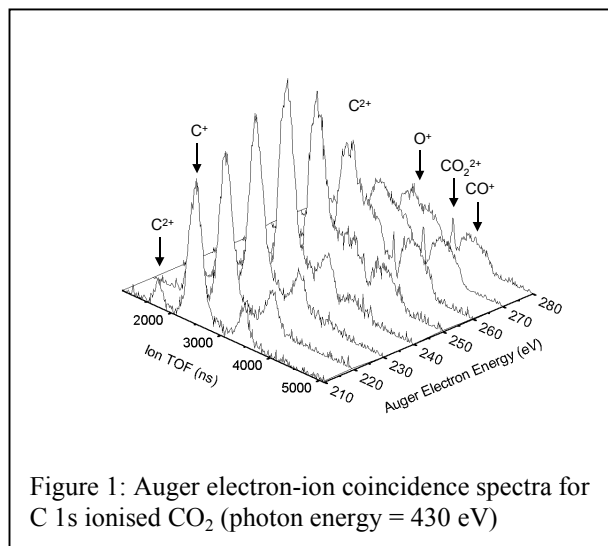


Figure 1: Auger electron-ion coincidence spectra for C 1s ionised CO₂ (photon energy = 430 eV)

Other data will be presented for the C 1s and O 1s edges and the C 1s $\rightarrow\pi^*$ resonance and the results compared with an earlier study on near threshold phenomena in core excited CO₂ [4]. In particular further details of fragmentation dynamics will be discussed in the light of triple coincidence experiments revealing ion pair correlations.

This work was carried out on beamline 5U.1 of the SRS, Daresbury Laboratory, United Kingdom and has been supported by the Engineering and Physical Science Research Council.

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Interchannel interaction vs. relativistic effects: the Xe 5p photoionization case

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Xenon 5p subshell photoionization has been studied in the vicinity of the Xe 4d shape resonance by angle and spin resolved photoelectron spectroscopy. Both kinds of spin polarization, transferred and dynamical, were determined between 40 eV and 150 eV. Dipole matrix elements and relative phase shifts derived from these experimental data are compared with calculations with regard to the strength of interchannel and relativistic interactions. The comparison shows strong influence of interchannel interactions on the transition matrix elements, particularly on the phase shift in the vicinity of the 4d shape resonance, but gives little evidence for relativistic interactions of comparable strength. This shows the persistence of LS coupling for continuum electrons in the presence of a shape resonance for a heavy atom like xenon.

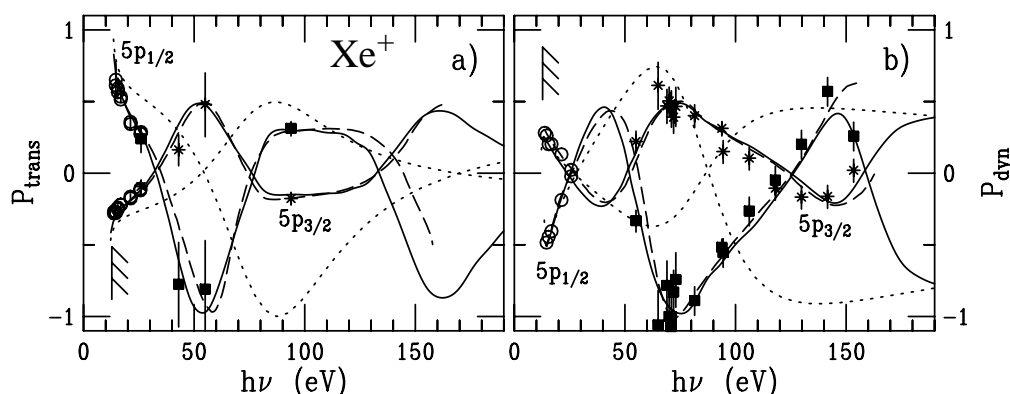


Figure 1: a) Transferred and b) dynamical spin polarization (see Ref [1]) of the Xe 5p photoionization lines shown as function of the incident photon energy. \circ Ref[2,3], ($5p_{1/2}$: \blacksquare , $5p_{3/2}$: $*$) - present measurements; dashed lines: relativistic RRPA Ref.[4]; solid and dotted lines: our nonrelativistic RPAE and HF calculations, respectively, using the code from Ref[5]).

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Absolute photoionization cross section measurements on atomic ions

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A merged ion-photon beam experiment is now in operation at the ASTRID storage ring in Denmark, installed on the undulator beamline and providing high intensity well collimated radiation over the photon energy range 25 —180 eV. By measurement of the overlap between ion and photon beams, and calibration of ion and photon detectors, cross sections with a precision of –10% have been measured for a range of ions of astrophysical interest. For the lighter ions, eg C⁺, the results have been compared with calculations from the IRON [1] and OPACITY projects [2].

We present here our measurements on the ions of Mg and Al, which we have used both to revise spectral assignments made earlier in the literature and also to compare with RPAE [3] and our own MCHF calculations. The ability to provide values of the oscillator strength has proved very useful in making these assignments, as well as making direct comparisons along the isoelectronic sequence Na, Mg⁺ and Al⁺⁺. The identification of the numbered resonances shown in the figure below will be presented in detail on the poster presentation.

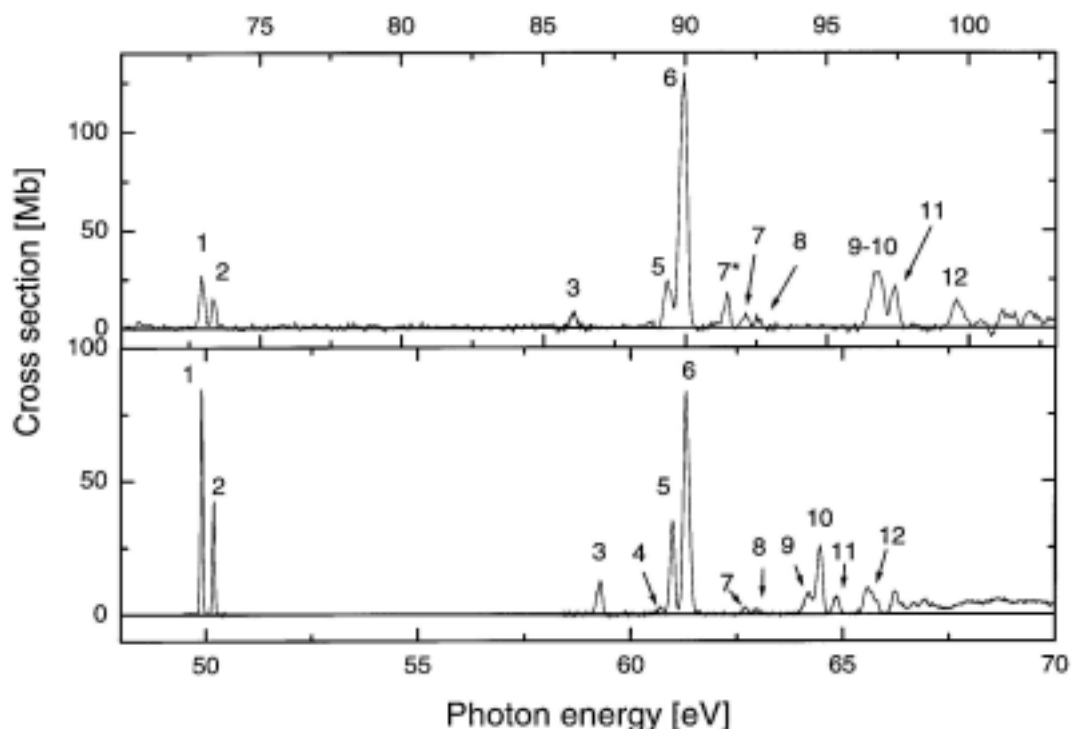


Figure 1: The absolute photoionization cross sections of Mg⁺ (lower) and Al⁺⁺ (upper). The numbers refer to the corresponding 2p —ns, nd transitions.

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EFFECTS OF LIGHT POLARIZATIONS ON $2s_g$ PHOTOELECTRON ANGULAR DISTRIBUTIONS FROM ORIENTED N_2 MOLECULES

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To perform complete experiments of molecular photoionization, we have measured the angular distributions of $2\sigma_g$ photoelectrons from oriented N_2 molecules using three different polarization states of incoming photons with 58.2eV, i.e., linear, left-elliptical and right-elliptical polarization.

Experimental results on the photoelectron angular distributions are shown in Figure 1. The molecular axis is aligned to the vertical line, and the polarization ellipse is indicated in the figure. These photoelectron angular distribution patterns can be expressed by the dipole matrix elements, phases, and Stokes parameters describing the polarization state of incoming light. Because we have determined the Stokes parameters before or after the measurements of the photoelectron angular distributions from fixed-in-space N_2 molecules, the unknown parameters are the dipole matrix elements and phases. Taking $p\sigma$, $p\pi$, $f\sigma$, and $f\pi$ partial waves into account, we have analyzed our photoelectron angular distribution patterns. Fitting curves are shown in the figure. To determine the unique solution of the matrix elements and phases, we have examined the solutions obtained for three different data sets; each data set gives more than two solutions. In this procedure, we have succeeded in picking up the unique solution, i.e., the common solution for the different data sets. The dipole matrix elements and phases determined uniquely by the complete experiments will be compared with the results by RPA calculations.

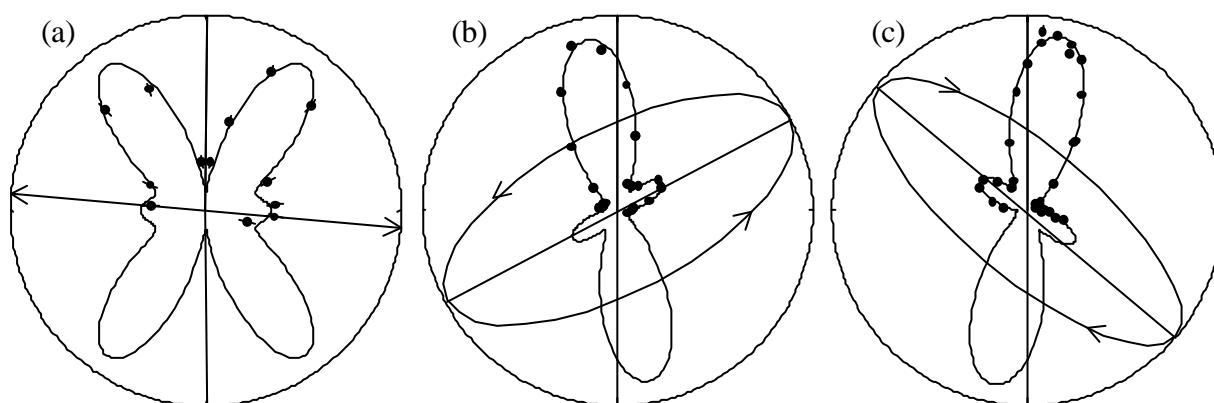


Figure 1: $2\sigma_g$ photoelectron angular distributions from fix-in-space N_2 ;
(a) linear polarization, $S_1=0.97$ (b) left-elliptical polarization, $S_1=0.42$
(b) and $S_3=-0.91$ (c) right-elliptical polarization $S_1=0.50$ and $S_3=0.87$

NONDIPOLE EFFECTS IN CORE-ELECTRON PHOTOEMISSION ANGULAR DISTRIBUTIONS OF SMALL MOLECULES

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Much of our understanding of the photoionization of matter is based on the electric-dipole approximation. It is generally known this approximation breaks down for photon energies above a few keV, as has been experimentally found [1], but it has been assumed the nondipole contributions to the photoionization matrix elements can be neglected for wavelengths in the soft x-ray and ultraviolet regions of the electromagnetic spectrum. However, recent experiments and theoretical developments have shown that significant nondipole effects occur for atomic [2] and molecular [3] photoemission at much larger wavelengths than expected. In the soft-x-ray regime, the first-order effects are predicted to be the major deviations for photoionization. First-order deviations from the dipole approximation for photoemission only affect the angular distribution of photoelectrons, not the cross section, and manifest themselves in a forward/backward asymmetry relative to the photon direction.

Here, we report observations of significant deviations from the dipole approximation for the angular distribution of core-shell photoemission of CO₂, CF₄ and SF₆. For all three molecules, strong effects are found in the near-edge region. Particularly SF₆ has a complex behavior, with rapid changes in the nondipole deviations over the t_{2g} and e_g continuum resonances above the S L_{2,3} edges. The measurements were performed at the Advanced Light Source synchrotron radiation facility at the Lawrence Berkeley National Laboratory. Four time-of-flight spectrometers, positioned both in and out of the plane perpendicular to the photon beam to make the nondipole-effect measurements possible, were used to record the photoelectron spectra [4].

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Ni 2p Photoabsorption and Resonant Photoelectron Spectroscopy of Molecular High-spin Ni complex, Ni(*N,N'*-dimethylethylenediamine)₂Cl₂)

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We found that some planar molecular Ni complexes with a 3d⁸ low-spin ground state show different resonant behaviors from Ni metal and Ni oxide [1]. The kinetic energy of Ni 3p satellite peaks decrease as the photon energy increases, indicating the one electron, or excitonic, feature of the excited states in these systems. In the present study, we have measured soft X-ray Ni 2p absorption and resonant Ni 3s and 3p photoelectron spectra of a molecular Ni complex with a 3d⁸ high-spin, Ni(*N,N'*-dimethylethylenediamine)₂Cl₂ (Ni(DED)₂Cl₂) to clarify the effect of the spin state on the core-excited states of the system.

Measurements of X-ray absorption and photoelectron spectra were performed at BL1A soft X-ray beamline of the UVSOR facility in the Institute for Molecular Science. Figure 1 shows the kinetic energy for the Ni 3p and 3s primary ion states and the satellite peaks observed in the resonant photoelectron spectra as a function of the photon energy. This shows nearly linear relationship between the kinetic energy of these satellite peaks and the photon energy with the slope ($\Delta KE/\Delta h\nu$) of +1. This dependence of satellite bands on the photon energy is different from that of the low-spin complexes where the slope becomes negative (e.g. $\Delta KE/\Delta h\nu = 0.55 \pm 0.05$ for K₂[Ni(CN)₄] [1]), but is similar to that of NiO with important electron correlation and multiplet interaction. This indicates that the excited states in this high-spin Ni complex cannot be described within the one-electron picture. A series of our studies on the Ni complexes with various electronic states reveals that the resonant behavior of photoelectron spectra reflects the electron configuration of core-excited metal atom which depends on the chemical bonding state between the metal and the ligand molecules.

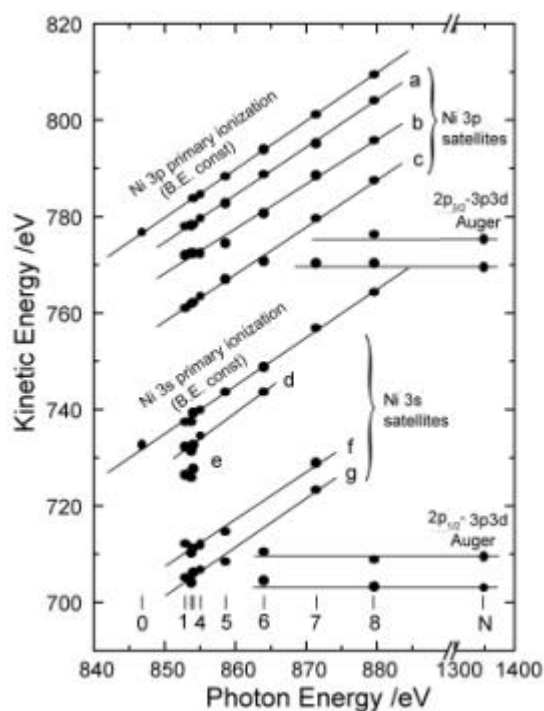


Fig. 1. Photon energy dependence of the kinetic energy for Ni 3p, 3s primary and satellite photoelectron peaks.

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PHOTOABSORPTION CROSS SECTIONS OF MOLECULAR CHLORINE

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The absolute total photoabsorption cross sections of molecular chlorine has been measured from ionization threshold to 30 eV using double electrode ion chamber and synchrotron radiation. The photoabsorption cross section shows three broad peaks at around 97, 92.5 and 85 nm superimposed to a continuous background. Also, small increase of photoabsorption cross sections were found at around 74, 60 and 53 nm. In general, the agreement between the present data and Samson's [1] one is excellent with maximum deviation of about 5% up to 83 nm. The earlier measurement by W.J. van der Meer et al. [2] was about 30% higher than the present one at 58.4 nm. It seems neither length nor velocity approximation in the Hartree-Fock calculation [3] provides satisfactory results for the photoionization of molecular chlorine. It is interesting that velocity approximations fits better in the lower energy side and length approximations in the higher energy side.

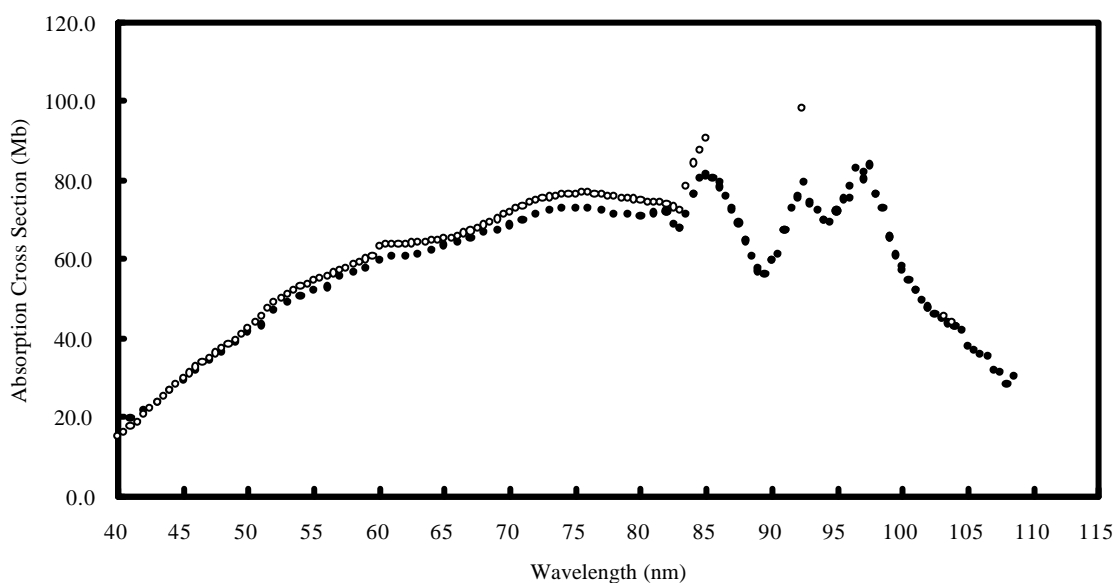


Figure 1. The total photoabsorption cross sections of molecular chlorine: Filled circle, present data. Open circle, the total photoabsorption cross sections measured by Samson et al. [1].

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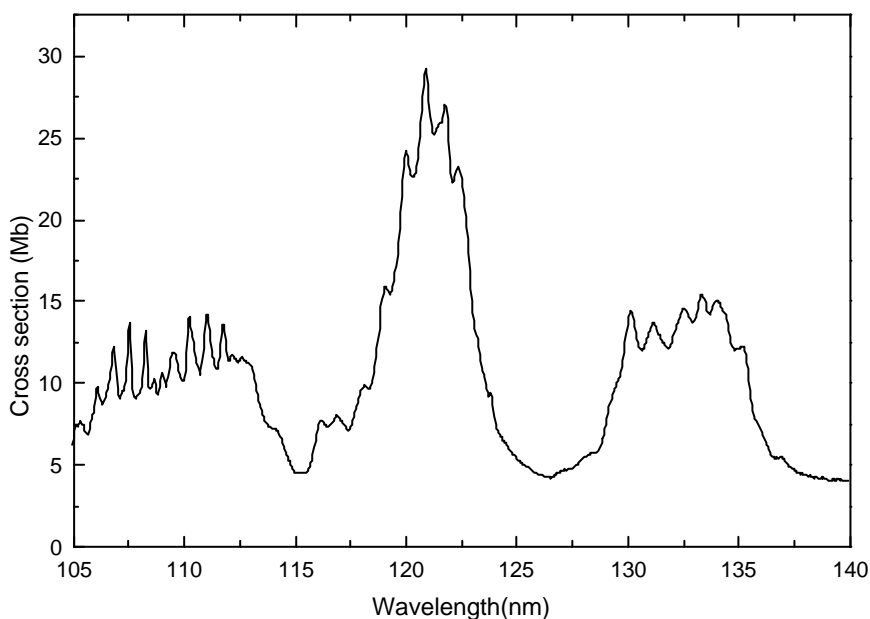
ABSORPTION CROSS SECTIONS OF O₃ IN VUV

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The absorption cross sections of O₃ in the 105-200 nm wavelength region were measured. Ozone was prepared by the silent discharge of oxygen and trapped in silica gel. Absorption cross sections were measured by flowing the purified ozone through the experimental system. Minor oxygen absorption bands were subtracted to derive the ozone spectrum.

The absorption spectrum of ozone in the VUV wavelengths consists of several regions. Between 155 and 200 nm, a low absorption spectrum was found. A region strong bands consists of several excited states was found at 105-140 nm. Two progressions of vibrational states were found between 113 and 105 nm. The structures in 105-108 nm, which are previously unknown, are similar to the other one in 108-113 nm. Our cross sections in $\lambda > 110$ nm are comparable to the previous measurements [1-2].



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SPIN-RESOLVED ELECTRON SPECTROSCOPY OF THE OCS MOLECULE

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Spin-resolved electron spectroscopy of atoms and molecules can yield valuable information about the dynamics of the photoionization and Auger decay processes as well as about the electronic structure of the samples. Quantum mechanically this information is expressed in terms of the wavefunctions for the initial and final states and the dipole and Coulomb transition matrix elements. A complete set of matrix elements, amplitudes and phase shifts, enables the prediction of all observable parameters of the emission process, such as the angular distribution and spin polarization of the electrons. For this reason, big advancements were made in complete photoionization experiments of atoms in recent years [1].

In contrast, there have been only very few studies of inner-shell photoionization of molecules beyond intensities and angular distributions [2]. A molecular ‘complete experiment’ is much more difficult than the determination of matrix elements for atoms, because of the large number of possible outgoing partial waves. Additionally, the molecular environment can influence the core orbitals of the atoms in the molecule. This can lead to the splitting of energy levels due to vibrations, lower than spherical symmetry of the system, etc.

Recently, Kukk et al. [3] investigated the sulphur 2p photoionization of OCS molecules by high-resolution, angle-resolved electron spectroscopy. They found that the angular distribution parameter β of the two molecular-field-split components of the sulphur 2p_{3/2} line differs significantly at a broad range of photon energies above the 2p threshold. Since the origin of this difference cannot be traced solely by angle-resolved spectroscopy, we measured the spin polarization of the S 2p lines. We used circularly and linearly polarized light of 185-220 eV photon energy from the new elliptical polarization undulator (EPU) beamline of the Advanced Light Source storage ring to carry out this experiment. The spin polarization component measured with linearly polarized light is almost zero for all lines of the spectra. In contrast, in the measurements with circularly polarized radiation the 2p_{1/2} line is almost completely polarized and the molecular field split components of the 2p_{3/2} line show clearly different degree of electron polarization.

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ANGULAR DISTRIBUTION OF 1s PHOTOELECTRONS FROM FIXED-IN-SPACE OCS MOLECULES

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To understand the mechanism of the shape resonance, we have measured the angular distributions of photoelectrons from C and O *K*-shells of the fixed-in-space CO molecules and determined dipole matrix elements and phase shift differences describing the photoionization process (*i.e.* perfect experiment) [1], [2]. However this kind of experiments has been done only for the diatomic molecules. There still has been a great distance to clarify the origin of shape resonance for polyatomic molecules. As a prototype of polyatomic molecules, we have selected OCS molecules and measured S-, C- and O-1s photoelectron angular distribution from them.

Figure 1 shows the angular distributions of 1s photoelectrons from fixed-in-space OCS molecules on the top of the shape resonances above the S, C and O *K*-edge. The angular distribution patterns for S, C and O *K*-shell are very different each other, as can be seen from the figure. It implies that the shape resonances in the S, C and O *K*-shell ionization continua are caused by different mechanisms, reflecting the different molecular potentials. As these angular distribution patterns are expressed by the dipole matrix elements and phase shift differences, we can determine them analyzing the experimental data. At the conference, we will present dipole matrix elements and phase shift differences, which are obtained by the same procedure of Ref. [2], and try to make the origin of the three shape resonances clear.

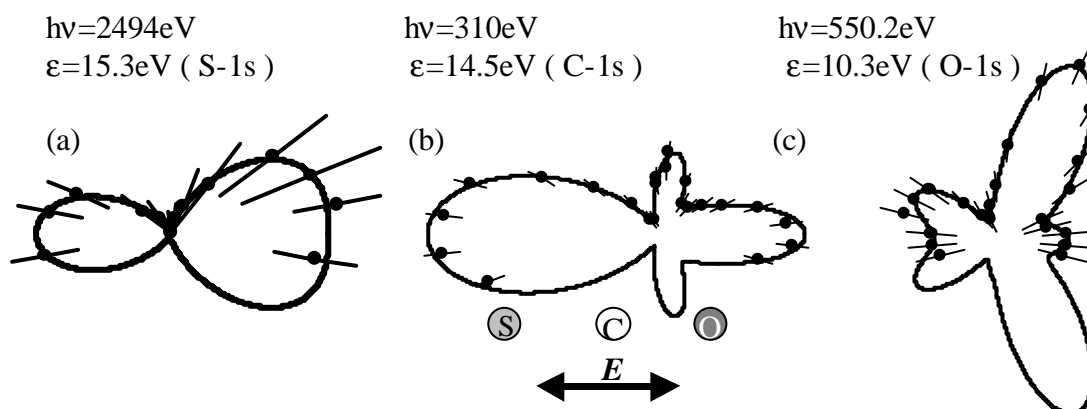


Figure 1: Polar plots of photoelectrons angular distributions (full circles) for the S (a), C (b) and O *K*-shell (c) of OCS. The electric vector of linearly polarized light is parallel to the molecular axis. Photoelectron kinetic energies (ϵ) are shown in the figure.

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Inner shell Photoabsorption in the chlorine iso-electronic sequence

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Photoionization is one of the fundamental processes in the interaction of photons and matter. Unfortunately detailed studies of the inner-shell photoionization exist only for a limited number of free atoms and ions. However, especially for ions these data is of great interest, due to their importance in astrophysics, as space is filled primarily with ionized matter. We present a study on the resonant 2p photoabsorption process of atomic chlorine, single ionized argon, doubly ionized potassium and triple ionized calcium. First experimental data on free chlorine atoms have been presented by Caldwell et al. [1]. A first theoretical study of the photoionization process for chlorine has been presented in [2]. For single ionized argon first experiments have been performed using an ion source installed at beamline 10.0.1.2 at the Advanced Light Source (ALS). Experimental data for higher ionized atoms are not available up to now.

The electronic structure in the chlorine sequence is comparable to argon, but with an unfilled 3p shell, so an absorption similar to the Ar 2p case, with relatively broad resonances ($\Gamma \approx 100$ meV) and a pronounced Rydberg structure is expected. However, the absorption of the open shell atom and ions is different. Here a large number of narrow resonances with linewidths around 10 meV are observed in the experiment. Above the first 2p threshold a strong broadening is observed due to a spin flip decay, which is not observed in the case of argon.

To analyze the photoabsorption process, we are using a theoretical approach based on the Hartree-Fock (HF) method and the extended Fano formalism. For the case of chlorine no clear Rydberg structure is visible in the spectrum, due to the strong mixing of the states. Nevertheless a good description of the experimental data is achieved. For Ar⁺ also a good description of the experimental data is found. Here the Rydberg structure is much more pronounced compared to chlorine, but the states are still mixed. This mixing has nearly vanished for K²⁺ and Ca³⁺ and an unperturbed Rydberg series of narrow resonances ($\Delta E \approx 10$ meV) is observed.

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High-resolution symmetry-resolved ion yield spectra of N₂ : double excitations near the K-shell threshold

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Recent work [1, 2] has revealed resonances below and just at the 1s threshold of N₂, which do not originate from singly excited states. These resonances were assigned to core hole double excitations. Although the double excitations in the continuum are easily observed in the normal absorption spectrum of N₂, the other doubly excited states may lie in the same photon energy region. It is highly desirable to decompose degenerate features in the absorption spectrum and to determine their excitation energy, intensity, line width, and symmetry.

The experiments were performed on the newly constructed beamline BL4B at the UVSOR, IMS. The fragment-ion yield spectra of N₂ were measured with two identical ion detectors having retarding grids, which were set at 0° and 90° relative to the electric vector of the light, by scanning the photon energy. The monochromator bandwidth was set to about 80 meV for a high-resolution mode.

The symmetry-resolved ion yield spectra of N₂ measured with a resolving power of about 5000 are shown in Figure 1. The I₉₀ spectrum reveals previously unresolved double excitations just above the K-shell ionization threshold and even on the σ* shape resonance position. The I₀ spectrum also exhibits double excitations around 415 eV. Their excitation energies and nature will be discussed with the help of theoretical calculations for the potential energy curves of the doubly excited states.

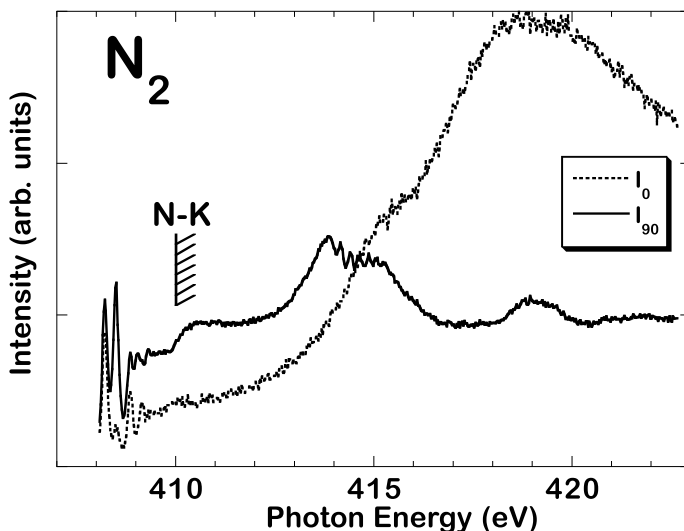


Figure 1: High-resolution symmetry-resolved ion yield spectra of N₂ in the K-shell ionization region.

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Fragmentation of state-selected SF₅CF₃⁺ probed by threshold-photoelectron photoion coincidence (TPEPICO) spectroscopy : the bond dissociation energy of SF₅–CF₃, and its atmospheric implications

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A recent paper (*Science* **2000**, 289, 611) has suggested that a new anthropogenic greenhouse gas, SF₅CF₃, recently detected in the Antarctic, has the highest radiative forcing per molecule of any gas in the earth's atmosphere. Using tunable vacuum-UV radiation from a synchrotron in the range 12-26 eV, we have measured the threshold photoelectron – photoion coincidence (TPEPICO) spectrum of this molecule. The ground state of SF₅CF₃⁺ is repulsive in the Franck-Condon region, the parent ion is not observed, and the onset of ionisation can only give an upper limit to the energy of the first dissociative ionisation pathway of SF₅CF₃ (to CF₃⁺ + SF₅ + e⁻). Using a variation of TPEPICO spectroscopy at high time-of-flight resolution to determine the kinetic energy (KE) released into the two fragments over a range of energies, however, we have extrapolated the data to zero KE to obtain a value for the first dissociative ionisation energy (DIE) for SF₅CF₃ of 12.9 ± 0.4 eV. A similar experiment for CF₄ (to CF₃⁺ + F + e⁻) and SF₆ (to SF₅⁺ + F + e⁻) yields values for their DIEs of 14.4₅ ± 0.2₀ and 13.6 ± 0.1 eV, respectively. We have therefore determined new values for the adiabatic ionisation energy of the CF₃ (8.8 ± 0.2 eV) and SF₅ (9.6 ± 0.2 eV) free radicals, for the enthalpy of formation at 0 K of SF₅CF₃ (-1753 ± 46 kJ mol⁻¹), and for the dissociation energy of the SF₅–CF₃ bond at 0 K (392 ± 48 kJ mol⁻¹ or 4.1 ± 0.5 eV). The implications of the bond strength for the lifetime of SF₅CF₃ in the earth's atmosphere are discussed. In addition, over the complete energy range of 12-26 eV, coincidence ion yields of SF₅CF₃ have been determined. CF₃⁺ and SF₃⁺ are the most intense fragment ions, with SF₅⁺, SF₄⁺ and CF₂⁺ observed very weakly. At threshold, SF₃⁺, SF₄⁺ and CF₂⁺ can only form in their lowest-energy dissociation channel, *i.e.* with CF₄+F, CF₄ and SF₆, respectively. Thus these fragment ions can only form following migration of a fluorine atom across the S–C bond. The translational KE release into CF₃⁺ + SF₅ are also measured at photon energies between 14 and 19 eV, and the results discussed in terms of different dissociation mechanisms of the ground and excited states of SF₅CF₃⁺.

POTASSIUM 2p PHOTOELECTRON SPECTRA OF GAS PHASE KCl

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The K 2p photoelectron spectra have been measured from molecular KCl sample, using synchrotron radiation at beamline I411 at MAX-II laboratory in Lund (Sweden), equipped with a modified Zeiss SX-700 plane grating monochromator. The spectra were recorded with a Scienta SES-100 analyzer at the “magic” emission angle of 54.7° and the sample was evaporated in a resistively heated oven at the temperature of about 600°C .

Figure 1 shows the K 2p photoelectron lines excited at 346 eV photon energy under the total instrumental broadening of about 630 meV. The main $2p_{1/2}$ and $2p_{3/2}$ spin-orbit split components are accompanied by an expanse of satellite transitions at the high binding energy side of the main structure. In order to clarify the origin and assignment of the observed transitions, multiple open-shell average-of-configurations Dirac-Hartree-Fock calculation combined with a small general active space configuration interaction (GASCI) calculation was carried out. The calculations have been performed using fully relativistic Dirac [1] program package. The resulting theoretical spectrum, convoluted with a 0.9 eV Gaussian and shifted by -0.85 eV, is also shown in Figure 1.

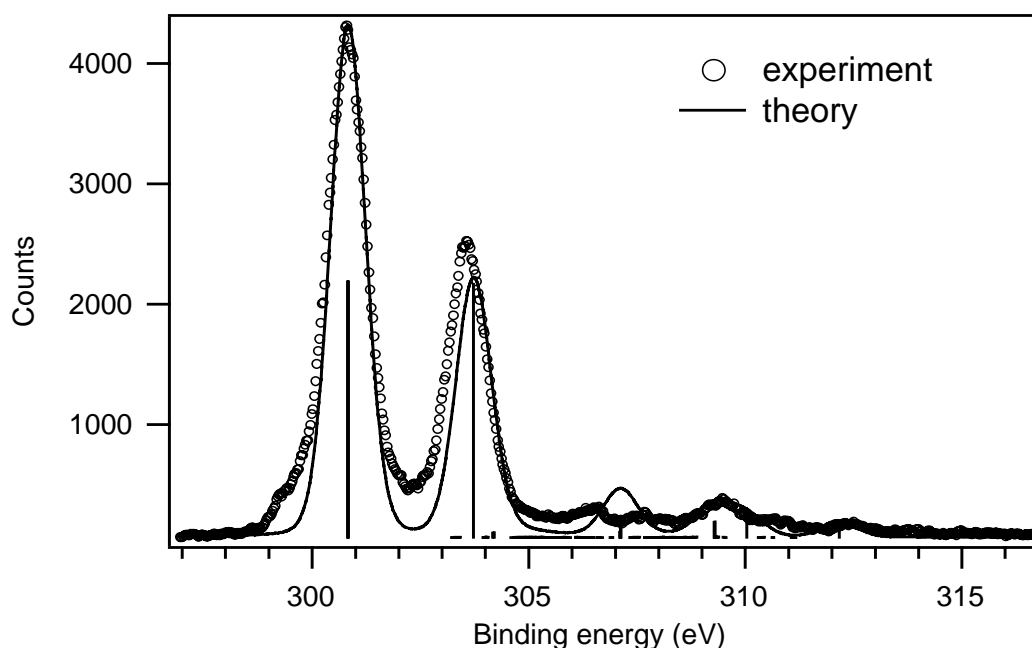


Figure 1. K 2p photoelectron spectrum of molecular KCl.

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FLUORESCENCE AND QUENCHING STUDIES FOR THE EXCITED STATES OF NO IN 160-220 NM REGION

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Production of the fluorescence from the excited states $A^2\Sigma^+$ ($v'=0-7$), $B^2\Pi$ ($v'=5-8$), $B'^2\Delta$ ($v'=0-2$), $C^2\Pi$ ($v'=0$), and $D^2\Sigma^+$ ($v'=0$) of NO in 160-220 nm wavelength region were investigated by using the VUV synchrotron radiation at SRRC as the excitation light source. The fluorescence in the VUV to infrared wavelengths was measured by using a combination of filters and photomultiplier tubes. Quenching rates were measured for gases He, Ar, N₂, O₂, CO₂, and CF₄. Some bands above the dissociation level was observe to emit at the increased buffer gases pressure conditions. These included bands of B($v'=9$), C($v'=1$) among others. Collision related processes were employed to explain these data.

AUGER-FINAL-STATE-DEPENDENT DISSOCIATION PROCESSES OF CORE-EXCITED ACETONITRILE

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Photochemical reactions of complex organic molecules induced by core excitation have been studied extensively in recent years [1]. Since core-excited organic molecules dissociate via various Auger-decay processes, dissociation processes are expected to depend on Auger-final state. A coincidence measurement of energy-analyzed Auger-electrons and fragment ions is, thus, a powerful tool to investigate such dissociation processes. Acetonitrile is a quasi-linear polyatomic molecule which has two different bonds of a C–C and a C≡N. We reported angle-resolved time-of-flight mass spectra of acetonitrile following N1s→π* excitation, previously [2]. In the present study, we have measured Auger electron-photoion(-photoion) coincidence (AEPICO) spectra of acetonitrile-d₃ (CD₃CN) for N1s→π* excitation to investigate the Auger-final states dependence of dissociation processes.

Measurements were carried out at the soft X-ray beamline BL8B1 of UVSOR using a cylindrical mirror type electron energy analyzer and a time-of-flight mass spectrometer. Electrons and ions were extracted by an electrostatic field of 40 V/cm.

Doubly-charged fragment CD₂CN²⁺ is observed in AEPICO spectra. It would be produced by autoionization from resonant-Auger-final states with single charge and D atom elimination. When the energy of resonant-Auger-final state is higher than the threshold of double ionization, initial momenta of fragment ions become larger because of coulomb repulsion between two fragment ions. To elucidate dissociation mechanism of doubly-charged ions, we have measured AEPICO spectra. A part of the AEPICO 2-D maps for the final-state-energy of 50 eV are shown in Fig.1. Coincidence peaks with a slope of –1 are observed not only for (D⁺/C₂D₂N⁺), (N⁺/C₂D₃⁺) and (CD₃⁺/CN⁺) but also for (CD₂⁺/DCN⁺) which produced with rearrangement. These ion pairs are produced by two-body dissociation. On the other hand, the slopes of (C⁺/CD₃⁺) and (D⁺/CD₂N⁺) peaks are about –2 and –0.7, respectively. These values are in good agreement with the calculated values for the sequential three-body dissociation processes as following.

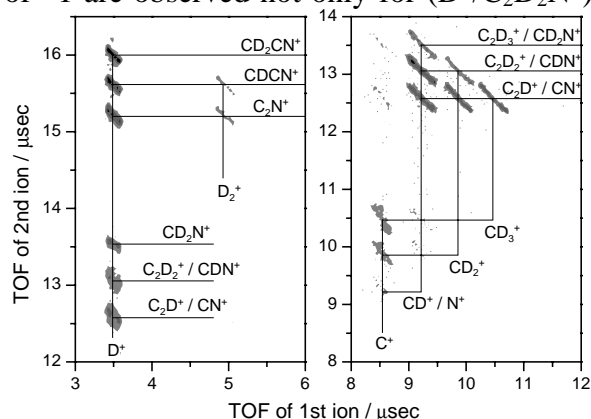


Figure 1: AEPICO 2-D maps of acetonitrile (CD₃CN)

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Detailed Analysis of the $2p^{-1} \rightarrow 3p\pi^{-2}$ Normal Auger Spectra in HCl and DCl

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Molecular normal-Auger spectra due to the decay of core-hole states to quasistable two-hole final states exhibit a rich vibrational fine structure. For core-hole states with angular momenta $l > 0$ (i.e. p and d holes) the spectra can be influenced by spin-orbit and ligand-field splitting. These splittings as well as vibrational splittings of the core-hole state lead to lifetime interference contributions and result in highly complicated spectra.

Recently, we performed a detailed analysis of the $3d^{-1} \rightarrow 4p\pi^{-2}$ normal-Auger spectra of HBr and DBr, where spin-orbit and ligand-field splitting as well as vibrational lifetime interference were properly taken into account for the first time, leading to a much deeper insight into the potential-energy surfaces of the states involved.

In the present study, we carried out a similar evaluation of the $2p^{-1} \rightarrow 3p\pi^{-2}$ normal-Auger spectra of HCl and DCl. For that purpose high-resolution Auger spectra of both HCl and DCl were measured at three photon energies using the undulator beamline I411 at MAX II storage ring in Lund, Sweden. The Auger spectra were fitted simultaneously with the $2p$ photoelectron spectra taken at the same photon energy; this allows to take the electronic lifetime interference into account semi-empirically. The equilibrium distances and vibrational energies of the final states $^3\Sigma^{-}$, $^1\Delta$, and $^1\Sigma^{+}$ are derived and compared with calculations, revealing good agreement. From the fits we also derived the intensity ratios of the different $2p^{-1} \rightarrow 3p\pi^{-2}$ normal-Auger transitions and the energetic splitting between the states $^3\Sigma^{-}$, $^1\Delta$, and $^1\Sigma^{+}$.

In addition we observed some spectral features in the Auger spectra that vary with the excitation energy. These spectral features are explained with the Auger decay of $2p^{-1}3p\sigma^{-1}\sigma^{*}$, $2p^{-1}3p\pi^{-1}\sigma^{*}$, $2p^{-1}3p\sigma^{-1}Ryd$ states that are resonantly excited at different photon energies.

ANGULAR CORRELATION BETWEEN ELECTRONS EMITTED IN DIRECT DOUBLE AUGER PROCESS

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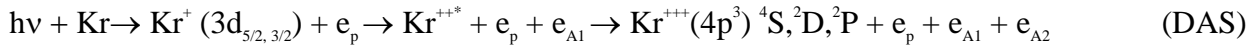
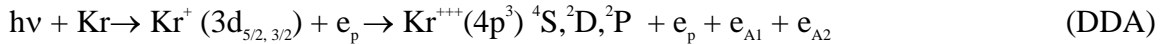
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Double photoionization may occur via a direct (D) or an indirect (I) process. The latter (I) is characterized by the formation of an excited state of the singly charged ion that may decay into the double continuum via Auger electron emission. The emission of the photoelectron and the Auger electron can be treated within a two-step model, made up by two uncorrelated successive processes. Except particular cases [1], the two-step model correctly describes the measurements. The direct transition (D) related to the dipole operator would not be possible without correlation in the initial and final state. It has been shown that electron-electron repulsion and the symmetry of the final state explain the main features of the angular spectra [2,3].

We here present results obtained in an experiment in which relaxation is now responsible for a simultaneous emission of two electrons. We have chosen the relaxation of a $3d_{5/2 \text{ or } 3/2}$ hole of Kr^+ leading to Kr^{+++} ion. This double Auger processes can occur via direct or indirect processes:



Angular correlations between the two Auger electrons A_1 and A_2 were studied by measuring both electrons in coincidence for a photon energy of 120 eV using synchrotron facilities of LURE. We tried to isolate the direct double Auger (DDA) from the sequential one (DAS). In a DDA process, one can assume that coulomb repulsion and symmetry effects determine the correlation like for (D), except that relaxation is, here, involved. For the selected final states, the symmetries of the Auger electron pair do not allow anti-parallel emission. Like for the direct double photoionization (D) of helium an angular node was expected in the back-to-back emission [2], but we did not clearly observed it. Contamination by others processes, like direct triple ionization, which in our case does not seem to be negligible, may explain this behavior. Theoretical calculations and interpretations are in progress.

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BEHAVIOUR OF LINEWIDTHS IN RESONANT AUGER AND CASCADE AUGER PROCESSES

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Resonant Auger spectra are well known to exhibit the linewidth–narrowing effect. Tuning the photon band width the resulting resonant Auger spectra can in principle be made to exhibit widths from zero (convoluted with the detector efficiency) up to the natural lifetime width. When the remaining ion permits a further Auger decay the second–step widths are in most cases determined by the natural width of the first–step final state. This happens when the resonant Auger electron has sufficiently large energy so that the second–step decay is decoupled from the resonant Auger emission [1].

In cases where the first–step and second–step spectra are at the same energy region it may be difficult to identify the peaks corresponding to the resonant Auger transitions from the second–step ones. One example of such a case is the cascade process following the $4d \rightarrow 6p$ excitation in Xe. The resonant Auger electrons corresponding to the $[\text{Xe}]5s^1 5p^5 6p^1$ ionic states overlap energetically with the second–step Auger electrons corresponding to the $[\text{Xe}]5p^4$ states. It is thus an interesting possibility to use the photon band widths to tune the width of the first–step peaks, while the second–step peaks are left untouched. This opens up the possibility to extract detailed information about the cascade process, which is known to be extremely sensitive to relativistic and correlation effects [2]. We present simulated and experimental spectra illustrating the process.

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The structure of water adsorbed on Cu(110)

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The interaction of water with surfaces is a key area of research, given the many associated chemical and biological processes that occur in nature. Water interacting with copper surfaces is complex system [1,2], since both the type of bonding with the surface and the probability of water dissociation, is not clear. Some previous work refer a dissociative adsorption process [1], while others claim to observe dissociation only under an oxygen precovered surface [2]. In isolating a monolayer coverage (ML) of water on the Cu(110) surface we hope to clarify the understanding of the water-Cu(110) interface.

We have used X-ray Photoelectron Spectroscopy (XPS) to study the uptake of water on Cu(110) surface using undulator beamline, I511, at Max-Lab synchrotron radiation facility in Lund, Sweden [3]. In order to prepare a well defined monolayer (ML), approximately 2ML of water were first adsorbed at 90 K and subsequently annealed to 160 K for 5 min. The O1s XPS spectra of the ML show two different chemical shifted peaks at 532.5 eV and 530.7 eV binding energies, indicating a clear evidence that two different species exist on the surface. (See fig. 1). The low binding energy species is interpreted as an OH species bonded both through the oxygen to the surface but also hydrogen bonded to other water molecules.

NEXAFS measurements have also been performed on different surface preparations, also a function surface orientation and excitation E vector, in order to probe in-plane and out-of-plane bonding contributions. The interpretation of the NEXAFS data is supported by preliminary *ab initio* calculations.

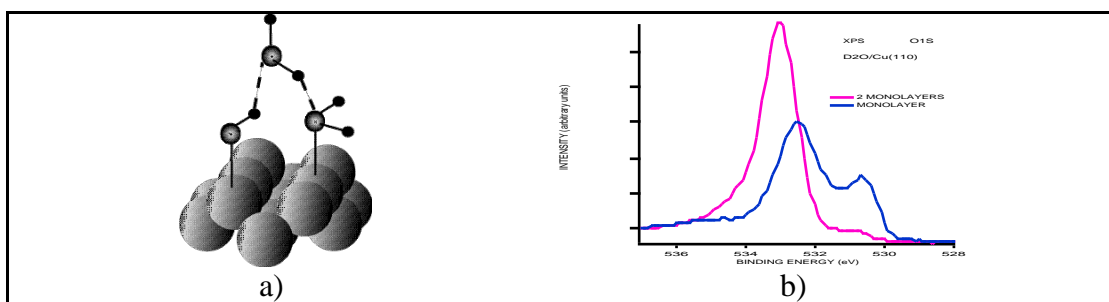


Figure 1: a) Adsorbed structure of water on Cu(110) surface and, b) corresponding XPS spectra.

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INTERFERENCE EFFECTS IN ANGLE RESOLVED AUGER- PHOTOELECTRON COINCIDENCE EXPERIMENTS

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The study of coherence is one among the most debated topics in quantum mechanics. Observations of such effects can be performed in atomic physics when the interaction between an atom and a photon or an electron proceeds through many undistinguishable channels leading to the same final state. Then, the experimental challenge is to achieve in both the exciting source and the analyzers a resolving power comparable with the width Γ of the involved intermediate atomic states. Such a resolution is mandatory to observe the interference effects typical of coherence.

Double photoionization of rare gases offers unique opportunities to investigate such interference effects. This process may, indeed, proceed either directly with the simultaneous emission of two photoelectrons, or indirectly with the sequential emission of a photoelectron and an Auger electron. As we will show in this poster, the latter process, characterized by the formation of an intermediate excited state of the singly charged ion that decays by Auger decay into the double continuum, is of particular relevance to the investigation of interference effects. In particular, two different cases have been investigated experimentally with the multicoincidence apparatus located at the Gas Phase beamline of the Elettra storage ring. In the first case, the photon energy has been tuned in order to obtain a photoelectron kinetic energy close to the Auger electron one [1,2]. In the second one, we have studied a process in which the same doubly charged final state can be reached via different paths which involve the population of two different intermediate states [3]. This latter case is analogous to the Young's classical two-slit experiments.

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High resolution resonant 2p–3d photoelectron and photoion spectroscopy of atomic Scandium

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The study of the resonant np – md photoionization especially of the transition metal elements and its neighbors in the periodic table has attracted very much interest for the last decades. The 3p–3d-excitation has been studied in great detail [1, and references therein]. In recent years the focus has switched to the study of the 2p– md excitation. Studies of the element Calcium (Ca) have shown that the resonant photoionization is very sensitive to the electron-electron-correlations of the outer electrons [2,3]. This contribution presents data on the neighboring element Scandium.

The experiments present were carried out at the BESSY II beamline U49-1/SGM in January 2000. Scandium (Sc) is evaporated in a Molybdenum crucible heated by electron bombardment. the resulting atomic beam is collimated and crossed with the linearly polarized undulator radiation. The photoions can be detected with a time of flight mass spectrometer. Alternatively the kinetic energy of photoelectrons emitted under the magic angle with respect to the main axis of the polarization ellipse of the synchrotron radiation can be analyzed in a hemispherical electron analyzer (SCIENZA SES200).

The experimental data are compared to theoretical calculations using a Hartree-Fock approach. The calculations treats the resonant photoionization as a two-step process calculating the excitation and the decay separate. The photoion yield spectrum as well as the photoelectron spectra show an excellent agreement with the calculated ones. The detailed analysis reveals that almost all oscillator strength is concentrated in the 2p–3d transition. Only one structure in the photoion spectrum can be assigned to $Sc^* 2p3d4s^24d$ states. The photoelectron spectra are dominated by lines assigned to highly excited states of the Sc II. It can be shown that the decay is dominated by a spectator process which leaves the originally excited electron unaffected.

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High Resolution Resonant Auger Raman Spectra of HBr

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Resonant Auger Raman spectra of atoms and molecules have been studied extensively due to the advances in the synchrotron light sources and high resolution electron energy analyzers [1,2]. The major advantage of the “resonant Auger” process over the normal Auger process is that the lifetime of the core excited state does not contribute to the experimental linewidth. The broadening and the complication due to the ligand-field effect commonly observed in d and f core level spectra can be eliminated in the resonant Auger spectra [3].

High resolution resonant Auger spectra of HBr are presented at the Br 3d to 5s, 5p, 6p and 7p resonances. The resonant Auger spectra subsequent to the 3d→5s and 3d→5p excitations can be described by the splitting of the $4p\pi^{-2}$ two-hole final states derived from normal Auger spectrum of HBr [4] and a coupling of the Rydberg electron to the final states, with little vibrational fine structure. However, the spectra due to the 3d→6p and 3d→7p excitations exhibit complex features. Surprisingly, these features can be described with a combination of the splitting of the $4p\pi^{-2}$ configuration into the final states $^3\Sigma^{-}$, $^1\Delta$, and $^1\Sigma^{+}$ and the vibrational profile obtained from the $3d^{-1}\rightarrow 4p\pi^{-2}$ normal Auger process [4]. We conclude that the equilibrium distance of the $4p\pi^{-2}$ 5s, 5p final states is close to that of the ground state and the 3d core-hole state, while the equilibrium distance of the $4p\pi^{-2}$ np (when $n\geq 6$) Rydberg states is close to that of the $4p\pi^{-2}$ two-hole states, i.e., the lower Rydberg states have a bonding character and the higher Rydberg states a non-bonding character.

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Alignment of Ar⁺ ions produced after resonant Auger decay of Ar* 2p⁵ 3d resonances

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The relaxation of the Ar* 2p⁵ (²P_{3/2}, ²P_{1/2}) 3d resonances is governed by the resonant Auger decay leading predominantly to singly charged ions with electron configurations Ar⁺ 3p⁴ 3d, 4d and 5d [1, 2]. In the present work dispersed fluorescence spectroscopy has been used to study the subsequent radiative decay of these excited ions. Similar to experiments on 4d excited Xe [3], the degree of linear polarization of the fluorescence was determined allowing to deduce the alignment of Ar⁺ ions produced after the resonant Auger decay. The experiments have been performed at the U49/1-SGM beamline of BESSY II using monochromatized synchrotron radiation with high degree of linear polarization. UV-visible fluorescence was investigated in the wavelength regime 320nm ≤ λ(flou) ≤ 530nm with a spectral resolution of about Δλ(flou) = 0.5nm.

A part of the fluorescence spectra is displayed in Figure 1 showing the variation of line intensities for different relative orientations between the polarization vectors of the fluorescence and the synchrotron radiation. The spectra are recorded after excitation of the Ar* 2p⁵ (²P_{3/2}) 3d resonance at hν(SR) = 246.9 eV and show mainly transitions of the type Ar⁺ 3p⁴ 4d → 3p⁴ 4p and 3p⁴ 4p → 3p⁴ 4s. The negligibly small differences for lines arising from initial states with total angular momentum J = 1/2 demonstrate qualitatively the consistency of our results. A detailed analysis of the data, taking into account also contributions from possible radiative cascades, is under progress and will be presented at the conference.

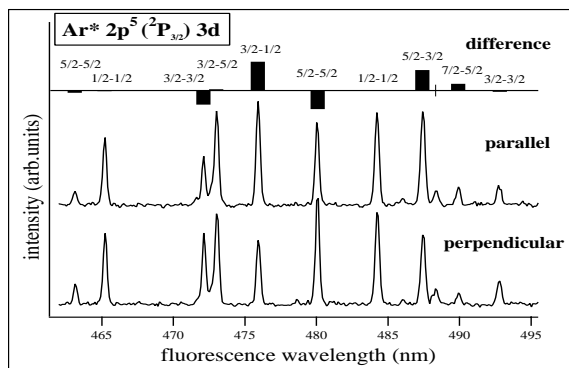


Figure 1: Part of two dispersed fluorescence spectra recorded after resonant Ar* 2p⁵ (²P_{3/2})3d excitation for parallel and perpendicular orientation between the polarization vector of the fluorescence and the synchrotron radiation. The differences between the intensities of the individual lines are given as a histogram on top of the figure.

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Coupling between the vibrational modes of core-excited and valence ionized states in CO₂ and N₂O

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Fluorescence spectroscopy in the wavelength region $200\text{nm} \leq \lambda(\text{fluo}) \leq 1000\text{nm}$ has been used to probe the vibrational structure of CO₂⁺ and N₂O⁺ outer valence states, which are produced after electronic relaxation of core-excited resonances. The experiments have been performed using monochromatized synchrotron radiation from the high-resolution beamlines U49-1-SGM (BESSY II) and BW3 (HASYLAB). The small bandwidth of the exciting photons allows to select different members of the strongly overlapping vibrational states of 1s-π* resonances, which are not completely resolved due to lifetime broadening. The spectral analysis of the fluorescence has been performed with a high-resolution spectrograph (Jobin-Yvon HR460, aperture f / 5.3) providing a maximum spectral resolution of $\Delta\lambda_{\text{FL}} = 0.03\text{nm}$.

Similar to earlier studies on vibrational resolved fluorescence of N₂⁺ after 1s-π* excitation [1], in the present work the coupling between the vibrational modes of core-excited and valence-ionized states of CO₂ and N₂O has been investigated. The high spectral resolution enables us to resolve the very close lying vibrational states of the tri-atomic molecules [2]. In the case of N₂O, the radiative relaxation N₂O⁺ A ²Σ (n₁,n₂,n₃) --> X ²Π (n₁,n₂,n₃) formed upon N-1s and O-1s excitation has been observed showing a strong enhancement of the bending modes of the N₂O⁺ A ²Σ state upon excitation at the low energy side of the 1s-π* resonances. For CO₂, the complex structure of the C₂O⁺ A ²Π (n₁,n₂,n₃) --> X ²Π (n₁,n₂,n₃) displays also pronounced variations of the relative intensities of the lines, when the photon energy of the exciting synchrotron radiation is tuned across the C 1s-π* resonance. For both molecules the importance of bending modes, excited due to the Renner-Teller effect, has been emphasized upon 1s-π* excitation [3, 4]. The analysis of fluorescence spectra allows to obtain detailed complementary information on the symmetry of the excited inner-shell resonances and its influence on the valence shell ionization.

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STATE- AND SITE- SELECTIVE DISSOCIATION PROCESSES OF CORE-EXCITED METHANOL

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Pronounced state-selective H_2^+ formation from H_2O molecule following the O 1s to the $2b_2$ resonant excitation has been reported by Piancastelli et al.[1] They also observed H_3^+ formation from core-excited methanol (CH_3OH) [2], though state selectivity in H_3^+ formation was not concluded. Also reaction pathway, whether H_3 formed by elimination from methyl group or by head and tail (H_3C and OH) reaction, was still not clear. To elucidate details of the dissociation mechanism of the core-excited methanol molecule, especially for the H_3^+ formation, high-resolution ion-yield spectra of photofragment ions by using photoelectron-photoion coincidence (PEPICO) and ion-pair correlation spectra by using photoelectron-photoion-photoion coincidence (PEPIPICO) were measured for CH_3OH and CD_3OH . PEPICO and PEPICO measurements were carried out at the BL8B1 beamline of UVSOR and the BL27SU of SPring-8, respectively.

As only D_3^+ is observed for core-excited CD_3OH , the reaction pathway to form H_3^+ (D_3^+) is concluded as the molecular elimination from the methyl group. This result was further supported by the existence of the D_3^+/COH^+ ion-correlation peak in the PEPICO spectra. Figure 1 shows the high-resolution partial ion-yield spectra of D_3^+ , COH^+ , CD_3^+ , OH^+ and total ion-yield spectra of CD_3OH in the C 1s ($3sa'$, $3pa''$) region. Partial ion-yields of D_3^+ and COH^+ , formed by C-D bond scissions, are lower at the $3sa'$ resonance than those at the $3pa''$ resonance. On the contrary, CD_3^+ and OH^+ formed by the C-O bond scission are stronger at the $3sa'$. Another interesting state- and site- selectivity for O-H bond scission was found in the O 1s region. In the O 1s excitation, suppression of OH^+ and COH^+ while enhancement of O^+ and DCO^+ relative to the total ion-yield are observed at the $3sa'$. This excited state selectivity for the O-H bond scission is not observed in the C 1s excitation at all. Therefore, the O-H bond scission is not only state-selective but also the site- (excited atom-) selective reaction.

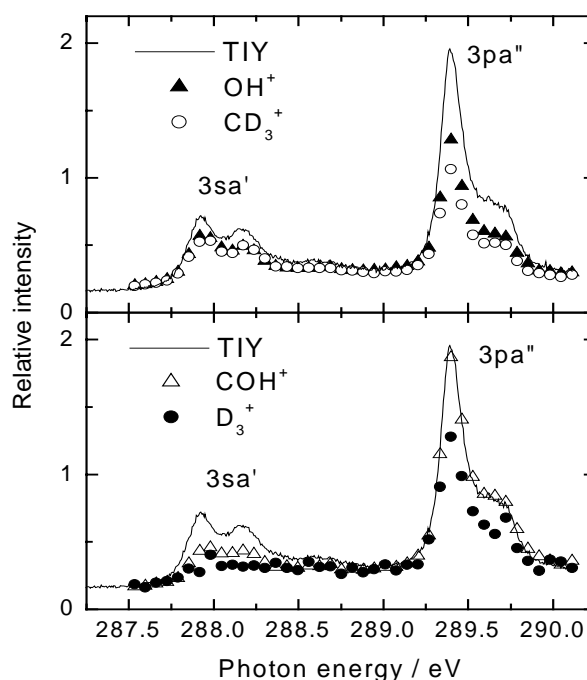


Figure 1. H_3^+ , COH^+ , CD_3^+ , OH^+ and total ion-yield spectra of CD_3OH in the C 1s ($3sa'$, $3pa''$) region.

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Study of Auger Decay Process and Subsequent Ion Desorption Reaction of Some Simple Molecules Using Molecular Orbital Theory

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Recent progress in synchrotron radiation techniques in a soft x-ray region has developed various newly experimental approaches. Especially the Auger electron - photoion coincidence (AEPICO) spectroscopy is one of powerful technique to investigate the Auger stimulated ion desorption (ASID) mechanism of core excited molecules, as it clarifies the Auger decay process (i.e. Auger final state) and the ion desorption mechanism related to the Auger process [1,2]. In this study, in order to elucidate the experimental results of AEPICO spectroscopy in detail, the Auger transition probabilities and dissociation factors for bonds were calculated using molecular orbital (MO) theory.

Because of the difficulty in exact calculation of the Auger transition probability and the applicability for various molecules, the calculation was based on the single configuration state function (CSF) and limited configuration interaction (CI) methods. The probability was estimated by the overlap between core and valence MOs using electron densities of valence MOs on the excited atom [3]. The bond dissociation factor was calculated as the product of the change of electron densities on the bond and the Auger transition probability in order to elucidate the result of the AEPICO experiment.

Figure 1 shows the calculated Auger transition probability and bond dissociation factor for H₂O molecule with the experimental normal Auger and AEPICO yield spectra as an example. The calculated probability well-reproduces the Auger electron spectrum. The correspondence between the bond dissociation factor and AEPICO yield spectrum indicates that the H⁺ ion desorbs efficiently from the Auger final states where two holes are produced in the bonding MOs. The suitability of this calculation including spectator Auger transition is also confirmed for H₂O, NH₃ and CH₃CN molecules and the ASID mechanisms are discussed for each molecule.

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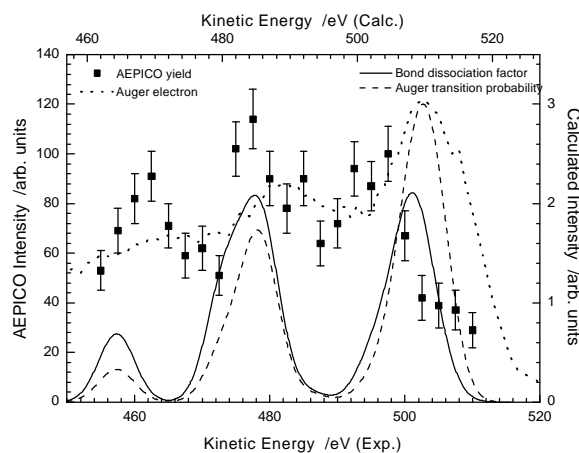


FIG. 1. Calculated and Experimental Spectra of core excited H₂O. Symbols: broken line; Auger transition probability, thick line; bond dissociation factor for OH, dotted line; normal Auger spectrum, and square; AEPICO yield spectrum for H⁺ ion.

K-SHELL PHOTOIONIZATION OF O₂ AND N₂ STUDIED BY FIXED-MOLECULES PHOTOELECTRON ANGULAR DISTRIBUTIONS

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In order to understand the 1s photoionization dynamics of molecules, the angle-resolved photoelectron-photoion coincidence (ARPEPICO) technique [1] has been applied to the 1s photoionization of O₂, in which there is no shape resonance enhancement in contrast to the 1s photoionization of N₂. The previous measurement of the angular distribution patterns (ADP) of 1s photoelectron of N₂ reveal that the 1sσ_g → fσ_u channel has a primary role in the σ* shape resonance [1,2]. On the other hand, there is no prominent feature above the O1s ionized threshold for O₂, so few attention to O1s photoionization dynamics of O₂ have been paid.

The residual O₂⁺ following the 1s photoionization has two multiplet states, the doublet and quartet states. In the present measurement, these states are not resolved. The ADP obtained with ARPEPICO is fitted with the Legendre polynomial (P_K) expansion to determine the relative values for those coefficients A_K . Assuming that the higher l ($l \geq 4$) partial wave are neglected, the square of the dipole matrix element for the 1s → fσ_u, $|D_{f\sigma}|^2$, is proportional to the coefficient A_6 . Roughly speaking, the value of $|D_{f\sigma}|^2$ very gently decreases as the incident photon energy becomes higher. However, the ADPs of the 1s photoelectrons remarkably change as a function of the incident photon energy. These results mean that the ADP is strongly affected by the phase shift and the relative intensities of the lower l ($l \leq 2$) component to the $|D_{f\sigma}|$.

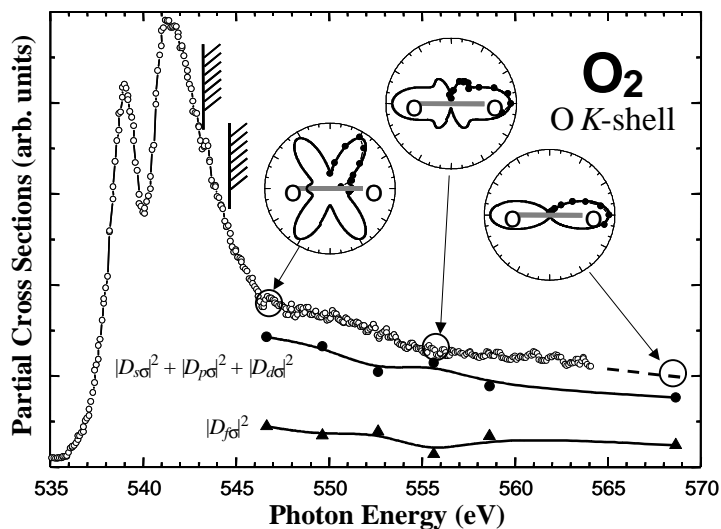


Figure Partial cross sections for the K-shell excitation and ionization of O₂. Open circles show the photoion yield observed in 0° direction respect to the electric vector of the incident light. Triangles and filled circles show the partial cross section for the 1s → εfσ_u transition and εsσ_g + εpσ_u + εdσ_u transitions. The inserted figures show the ADPs for O1s photoelectrons measured at $h\nu = 546.7, 555.7, \text{ and } 568.7$ eV.

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Non Franck-Condon effects in the photoionization of N_2 to the $N_2^+ A^2\Pi_u$ state and of O_2 to the $O_2^+ X^2\Pi_g$ state in the 19-34 eV photon energy region

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Photoionization to the $N_2^+ A^2\Pi_u$ state and to the $O_2^+ X^2\Pi_g$ state is studied using photoelectron spectroscopy.

In the case of the N_2 molecule, the experimental vibrational branching ratios obtained for the first time in the 20-34 eV region for the $v = 0-3$ levels, show strong non Franck-Condon effects around 22 eV. Using *ab initio* many body perturbation theory, branching ratios for ionization to the $A^2\Pi_u$ state are calculated. This study indicates that the Franck-Condon breakdown in the photoionization of the $N_2 1\pi_u$ electron is due to autoionization from Rydberg and valence states of N_2 . In Figure 1, top panel, the solid circle-lines (-●-) indicate the R(D) and R(C) Rydberg series autoionizing to the $A^2\Pi_u$ state of the N_2^+ molecule. In the bottom panel, the solid squares (■) represent Non Rydberg Doubly Excited Resonances (NRDERs) of $^1\Sigma_u^+$ symmetry predicted in this region and the solid circles (●) represent NRDERs of $^1\Pi_u$ symmetry.

In the case of the O_2 molecule, the experimental vibrational branching ratios for $v = 0-3$ levels, which are obtained in the 19-31 eV region show strong non Franck-Condon effects. Using *ab initio* many body perturbation theory branching ratios, vibrationally resolved partial cross sections and total cross section for ionization to the $X^2\Pi_g$ state are calculated. Molecular states that autoionize to the $O_2^+ X^2\Pi_g$ state continuum are discussed. Photoionization of the $O_2 \pi_g$ electron is not fully explained by channel coupling effects and autoionization from known Rydberg series and valence states.

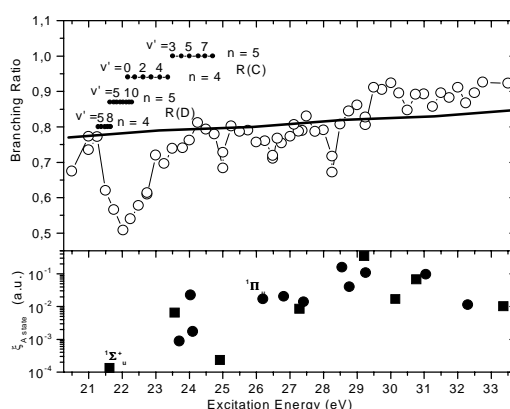


Figure 1. Top panel. Computed (—) and experimental (-o-) branching ratio for $v = 2$ over $v = 0$ of the $A^2\Pi_u$ state of the N_2^+ in the studied region. Lower panel. Computed autoionization strengths to the A state for the predicted NRDERs.

High-resolution inner-shell studies of free radicals and transient species.

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Third generation SR undulator beam lines allow low density and highly reactive species to be studied in the gas phase using high photon energy resolution. Core-excited states in the OH and OD free radicals and the CS transient molecule have been investigated for the first time. In the case of the lowest O 1s excited state ($^2\Sigma^+$) of OH and OD, vibronic components have been clearly observed in the total-ion-yield spectra using time-of-flight mass spectrometry. Relative transition probabilities, excitation energies, and core-hole lifetimes have been measured accurately for the vibronic components of this state. Excited states at higher energies have been also observed. The free radicals have been produced *in situ* by the fast atom-molecule reaction $H(D) + NO_2 \rightarrow \underline{OH}(\underline{OD}) + NO$ using a microwave technique to generate the H atom. In the case of CS, C 1s and S 2p excited states have been observed. Some of them display a resolved vibrational progression. As for the S 2p excited states, the extent of the vibrational progression, and therefore the change in molecular geometry, varies largely depending on the specific resonant state. Spin-orbit and molecular field splitting effects in S 2p excitation processes are observed for the first time in a diatomic molecule. The CS transient species has been produced *in situ* using the CS₂ precursor and the same microwave technique.

Core-excited states of transient and radical species are often observed as “intermediate fragments” in studies of ultra-fast dissociation processes of core-excited molecules. Our experiments provide, for the first time, a direct information on the inner-shell spectroscopy of those fragments.

STATISTICAL PROPERTIES OF INTER-SERIES MIXING IN HELIUM: FROM INTEGRABILITY TO CHAOS

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Due to the non-integrability of the classical three-body problem, no exact quantum numbers can be found to describe the helium atom. Nevertheless, for not too high excitation energies, the approximate classification scheme N, K_n (with N (n) being the quantum number of the inner (outer) electron and K the angular correlation quantum number) can be used to describe the $^1P^o$ doubly excited states in helium. However, in the semiclassical limit, i.e. close to the double-ionization threshold, the influence of the underlying classical phase space is expected to become more and more important for the quantum mechanical solution.

We present high-resolution photoabsorption spectra below the $N=9$ ionization threshold measured at beamline 9.0.1 at the Advanced Light Source in Berkeley/California, and calculated photoionization cross sections in the same energy region using the complex-rotation method. Based on the excellent agreement between experiment and theory, we performed a statistical analysis of the nearest neighbor spacing (NNS) using the theoretical results.

The NNS distribution was determined by two different procedures: (i) globally by considering all resonances regardless of the series to which they belong; (ii) individually for each series associated with a given value of $N - K$, i.e. constant number of bending quanta with respect to a collinear eZe configuration. In the first case the NNS distribution reveals a Poisson distribution that is typical for a regular system, while in the second case a development of the NNS distribution towards a Wigner distribution – which is typical for chaotic systems – was found. This corresponds to the loss of the radial quantum number N , whereas $N - K$ remains approximately a good quantum number, and it is directly related to the instability of the eZe orbits along the radial direction and their stability with respect to bending.

In addition, 1 dimensional (1D) stretched helium was studied theoretically below the $N=9$, 13, and 17 ionization threshold revealing that the NNS distribution develops clearly towards a Wigner distribution with increasing N . This study provides an estimate for the observation of a fully chaotic regime in 3D helium (for $N \geq 17$).

In conclusion, we show clear evidence of chaotic effects in both the 3D and 1D helium spectra on the basis of statistical analysis, emphasizing the role played by mixing between different Rydberg series.

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Ultra-fast dissociation processes in poly-atomic molecules.

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Core-excitation processes can be induced in a molecule if radiation of a suitable wavelength is used to promote one electron from a core level to an empty molecular or Rydberg orbital. Core-excited species are unstable and decay processes follow rapidly; the most long-lived core holes have a lifetime in the order of 10 fs. Core excitations lead frequently to dissociative or predissociative states. In some cases, the nuclear dynamics is so rapid that dissociation takes place on the same time scale as Auger electron emission. Ultra-fast dissociation is a term used to describe dissociation taking place on a time scale comparable to that of the Auger decay placing it in the low femtosecond regime. This time scale corresponds to the shortest molecular dissociation times i.e. to the fastest existing chemical reactions. It has previously been shown to occur in a number of molecules such as HBr [1], HCl [2], H₂S [3], O₂ [4] and N₂ [5]. Since the beginning of the nineties, there has been a long-standing discussion on the possible occurrence of ultra-fast dissociation of core-excited water into O*H and H (* indicates core excitation) [6] which has been indicated in ion yield spectroscopy [7, 8]. However, for ammonia no conclusive evidence of this phenomenon has been presented previously.

We present direct evidence for ultra-fast dissociation of molecular water [9] and ammonia in connection to photo-excitation of the O1s→4a₁ and N1s→4a₁ resonance's respectively. The core-excited molecules are shown to dissociate into a core-excited fragment and a neutral fragment on a time scale comparable to the core hole lifetime, i.e. a few femtoseconds. This conclusion is based on a resonant Auger study and qualitative arguments concerning the dispersive behavior of the fragment versus the molecular lines while tuning the frequency of the exciting light around the resonance as well as ab initio calculations in the case of water.

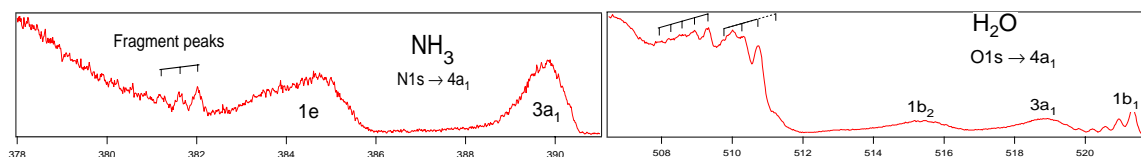


Figure 1. The Auger decay spectra of molecular water and ammonia after core excitation.

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Photoexcitation Processes of Methanol Isotopmers in VUV Region

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The photoabsorption cross sections of CH₃OH, CH₃OD, CD₃OH, and CD₃OD are measured in the 110-220 nm region using the synchrotron radiation light source in Taiwan. In the 160-220 nm region, the absorption maximum and band shape of CH₃OH are same as CD₃OH, and those of CH₃OD are same as CD₃OD; but the absorption maximum of CH₃OD is blue-shifted from CH₃OH. This result shows that the excitation is clearly related to the O-H bond. On the other hand, in the 140-160 nm region the absorption spectrum of CH₃OH is similar to CH₃OD, and that of CD₃OH is similar to CD₃OD; but the band origin of CD₃OH is blue-shifted from CH₃OH. This result shows that the excitation in this region is related to the C-O bond. Based on the absorption cross sections combined with theoretical calculations, the quasi-diatomic potential curves for the C-O and O-H bonds of methanol are derived.

The absorption in the 160-220 nm is a smooth continuous band that results a repulsive curve for the O-H bond. This curve is produced from perturbation between the 3s Rydberg state and the valence state that dissociates into CH₃O + H products. A vibrational progression with an irregular spacing appears in the 150-160 nm region. The irregularity is caused by perturbation between the 3p Rydberg state and the valence state that dissociates into CH₃ + OH products. A vibrational progression with a regular spacing appears in the 140-150 nm region. The upper state of this band is assigned to the 3p' Rydberg state of which the energy is higher than the repulsive valence state. The regular spacing indicates that this 3p' state is a bound state, and its potential curve is not perturbed by a valence state.

The deuteration technique is a powerful tool to study photoexcitation processes of molecules in the infrared region. The current results demonstrate that this technique can also be extended to study the photoexcitation processes in the VUV region.

The vacuum-UV photofragmentation of a range of hydrofluorocarbon (HFC) cations, $C_xH_yF_z^+$, studied using coincidence techniques

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HFCs are being increasingly used as substitutes for the banned chlorofluorocarbons in a range of domestic and industrial applications. The lifetime of these species in the atmosphere can be very long (*ca.* years) due to their slow reaction with the important tropospheric free radicals such as OH and O (1D). The removal of these species from the atmosphere can therefore be governed by processes occurring in the mesosphere. We are investigating these possible uni- and bi-molecular processes in the laboratory. The bi-molecular processes include reactions of HFCs with small positive ions and with electrons. The principal uni-molecular process is vacuum-UV photodissociation, especially with wavelengths in the range 50-150 nm, and this poster presents a progress report on our work.

Using vacuum ultraviolet radiation from the Daresbury synchrotron source, we have used threshold photoelectron-photoion coincidence (TPEPICO) spectroscopy to study the decay dynamics of the valence electronic states of the parent cation of several HFCs (CHF_3 , CF_3-CHF_2 , CF_3-CH_2F , CHF_2-CHF_2 , CF_3-CH_3) in the energy range 10 to 25 eV. This project represents a follow-on to a successful study of both saturated and unsaturated perfluorocarbon cations by the TPEPICO technique [1]. Electrons and ions are detected by threshold electron analysis and time-of-flight mass spectrometry respectively, allowing breakdown diagrams showing the formation probability of fragment ions as a function of the internal energy of the parent ion to be obtained. Higher resolution, fixed-energy TPEPICO spectra were also performed on many of the heavier fragment ions, and the translational kinetic energy released in fragmentation determined [2]. By comparing the integrated threshold photoelectron signal with the total ion yield as a function of photon energy, the importance of autoionisation in these molecules can be gauged.

For many of these saturated HFCs, the parent ions are not observed, indicating that the ground states of the ions are repulsive in the Franck-Condon region. Both from the analysis of the breakdown diagrams and the high kinetic energy releases, we conclude that non-statistical effects are occurring for states of these cations below *ca.* 18 eV. This suggests that decay from these states takes place rapidly before internal conversion to the ground state of the parent cation can occur. The substituted ethanes therefore seem to be mimicking the behaviour of $C_2F_6^+$ ($CF_3-CF_3^+$) where non-statistical effects are well known [1], and not that of $C_2H_6^+$ where statistical dissociation is observed [3]. F⁻-anion migration across the C-C bond must occur to explain the observation of some of the daughter ions.

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Resonant Auger Raman spectroscopy at the Kr 3p edge

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The x-ray absorption spectra of the sharp core levels of noble gases, Ne 1s, Ar 2p, Kr 3d, etc, have been extensively studied and are well understood [1, 2,] but less attention has been given to their broader, more difficult core levels [3, 4]. At the Kr 3p edge, the Rydberg states are about 1.4 eV wide, overlap one another and are superimposed on a strong 3d continuum [4]. Thus the peaks are difficult to identify and controversy exists about their assignment [5].

The $3p^{-1}nl$ ($n>4, l=0$; $n>3, l=2$) Rydberg states decay rapidly via Coster-Kronig (CK) processes to $3d^{-1}4p^{-1}nl$, $3d^{-1}4s^{-1}nl$ and related shake states, and via super Coster-Kronig processes. We have identified the CK states, fig. 1, and they lie close to the 3d satellite states $3d^{-1}4p^{-1}np$. On the first main $3p^{-1}nl$ resonance, there is a strong increase in emission below and above the 3d satellites. The peaks have widths determined by the resolution of the photons and the energy analysers, about 200 meV, fulfilling Resonant Auger Raman conditions. The new peaks disperse with photon energy as expected.

Constant Initial State spectra were measured by setting the analysers to energies corresponding to each group of peaks, fig. 2. The CIS spectra are shown in fig. 2, and clear differences in the resonant behaviour are seen. Peaks A, B and C show similar resonant behaviour on the absorption peak that has been attributed to the $3p^{-1}5s$, both for $3p_{3/2}$ and $3p_{1/2}$ at 209.8 and 218 eV photon energy respectively. In contrast the E and F multiplets show completely different resonances, and are assigned to ionic states derived from different intermediate excited states.

We have successfully applied the Resonant Auger Raman technique and CIS to the problem of the absorption spectrum of Kr at the 3p edge.

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Fig. 1. Photoemission spectra below resonance (lower curves), and on resonance below the Kr 3p threshold.

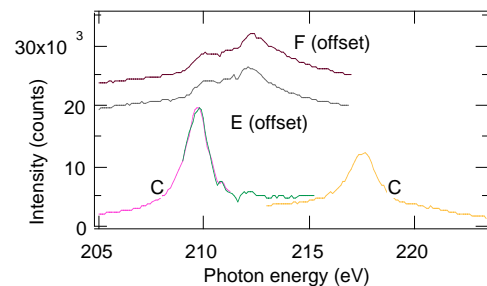
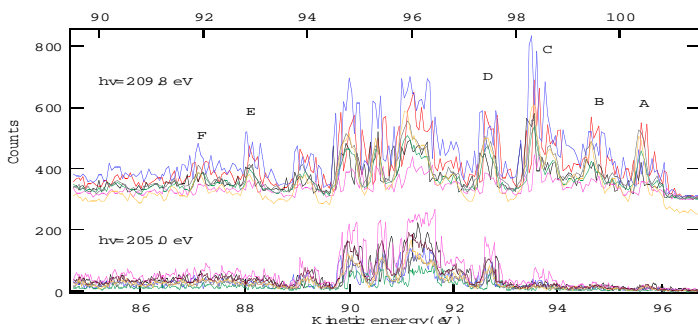


Fig. 2. CIS spectra, Kr 3p threshold.

High resolution photoabsorption studies at the C and O K edges

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We report the carbon and oxygen K edge x-ray absorption spectra of four tetrahedral molecules CX_4 ($X = H, Cl, F$) and a series of oxygenated organic molecules (CH_2O , $HCOOH$, CH_3CH_2O , CH_3COCH_3 , CH_3OH and CH_3OCH_3), with the cross-section determined in absolute units.

The antibonding valence peaks of the halides do not show any vibrational structure [1-3] but sharp Rydberg states are observed above these states at the C 1s edge. We identify a possible Fermi resonance in the Rydberg states of core excited CF_4 , and we report the CCl_4 Rydberg states for the first time. The C 1s intrinsic line widths were compared to theoretical predictions of ion state line widths and reasonable values are found for CH_4 and CCl_4 but not for CF_4 . The discrepancy is assigned to valence band - Rydberg mixing, which is especially strong in CF_4 , and/or to multi-centre Auger processes [4].

At the carbon K edge of the oxygenated species, most gases show vibrational structure; the spectrum of CH_2O is in good agreement with that of [5], whereas few high resolution spectra of the other gases have been reported. At the oxygen edge, only CH_2O shows vibrational structure. This is important as it indicates that for the very similar molecules CH_3COCH_3 and CH_3CH_2O , the structure is not absent due to lifetime broadening, but is obscured by many overlapping vibrational bands. This implies that the excited states of all aldehydes and ketones are most likely bound. On the other hand the situation is unclear for the saturated molecules CH_3OH and CH_3OCH_3 .

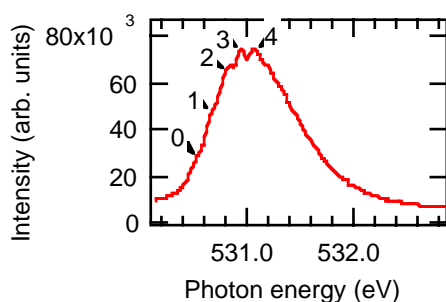


Fig. 1. Oxygen K edge spectrum of formaldehyde. The first 5 vibrational states (CO stretch) are marked .

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MEASUREMENTS OF THE ABSOLUTE PHOTOIONIZATION CROSS SECTION OF THE DOUBLY-CHARGED O²⁺ ION

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Photoionization of O²⁺ ion over the energy range 50-70 eV has been investigated experimentally using the end-station for studies of photon-ion interactions at the Super ACO synchrotron radiation source in Orsay. The experiments were performed at the SU6 undulator beamline, which provides monochromatic photon beams in the energy range 30-160 eV. The photon beam was merged with a collimated 500 nA-beam of O²⁺ ions produced in an ECR ion source. The spatial overlap of the beams was determined by three sets of translating-wire beam-profile monitors. After an interaction path of 20 cm, the parent O²⁺ beam and the O³⁺ product ions were demerged and counted separately. In the interaction region, the O²⁺ ions are mainly in the 2s²2p² ³P_{0,1,2} ground state, but some of them are also in the 2s²2p² ¹S or ¹D, and 2s2p³ ⁵S metastable states. Photo-ion yield measurements were carried out at a resolving power of 225. Previous R-Matrix [1] and new MCDF calculations were used to interpret the data.

In Fig. 1, we show the variation of the photoionization cross section as a function of photon energy between 47 eV and 65 eV. Continuum and resonant structures are seen in the measured cross section. The onset of the cross section at the 2p ionization threshold of the ³P ground state is clearly seen at 54.90 eV. The lines are produced mainly by autoionization of 2s2p²np (n ≥ 2) ²S+¹L_J excited states of O²⁺ ion into the continua of the 2s²2p O³⁺ ion. The results of both R-matrix and MCDF calculations agree satisfactorily with experiment and allow to identify the lines. Lines 1 and 2, below the ³P_{0,1,2} thresholds, are due to 2p-excitation of O²⁺ ions in the 2s2p³ ⁵S and 2s²2p² ¹S metastable states, respectively.

Above the ³P thresholds, several lines (line 3 at 58.27 eV as the first one) originate from excitation of O²⁺ ions in the ³P_{0,1,2} ground state. Other lines are due to similar excitations of O²⁺ ions either in the ¹D (line 4 at 58.90 eV) or ¹S (line 5 at 61.07 eV) metastable states. We determined also the absolute value of the cross section for photoionization into the continuum. Experimental and theoretical values of energies and cross sections will be presented and discussed at the conference.

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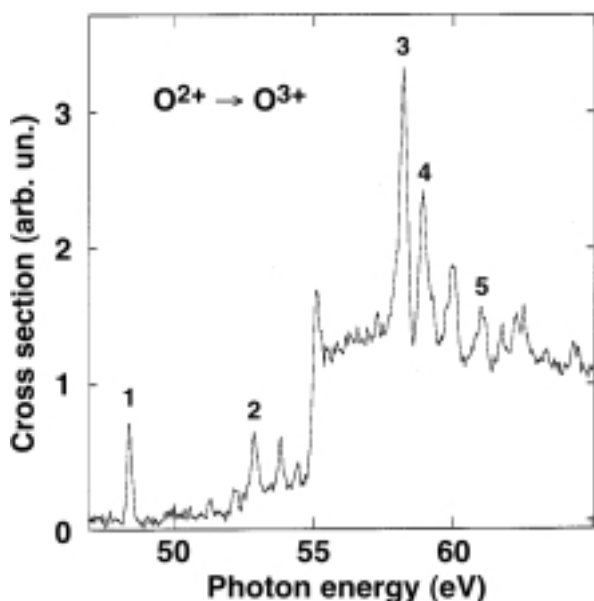


Fig. 1 - Measured photoionization cross section of O²⁺ between 47 and 65 eV photon energy. The cross section scale is in arbitrary units.

HIGH-RESOLUTION STUDIES OF CORRELATION SATELLITES IN PHOTOIONIZATION OF SODIUM ATOMS IN THE 2p-SUBSHELL

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In earlier studies of photoionization of sodium using electron spectroscopy, [1, 2] the many components of the various groups of satellites could not be resolved because the spectral and electron spectrometer resolutions were not good enough. In the work presented here, we have used the high-resolution Scienta electron spectrometer with an ultimate spectral resolution of 25 meV, and the photon beam available at the 10.0 1 beamline of the Advanced Light Source in Berkeley between 50 and 110 eV photon energy. The total instrumental resolution, including contributions from both excitation and detection channels as well as the Doppler effect, was at best 35 meV FWHM. With such a high-resolution, we were able to study the dynamics of 2p-photoionization transitions to correlation satellite states created without transfer of angular momentum: $\Delta l = 0$ (electronic configuration $2p^5 4s$, shake-up transitions) and with transfer of angular momentum: $\Delta l = 1$ (electronic configuration $2p^5 3p$) and $\Delta l = 2$ (electronic configuration $2p^5 3d$).

In the photoelectron spectrum following photoionization in the 2p-subshell, three groups of lines are clearly identified: the main lines due to single ionization of a 2p-electron, $\Delta l = 0$, ($2p^5 3s$ final ionic states), the satellites produced with $\Delta l = 1$ (states with $2p^5 3p$ electronic configuration), and the high-energy satellites produced with $\Delta l = 0$ (states with electronic configuration $2p^5 4s$), and $\Delta l = 2$ (states with electronic configuration $2p^5 3d$). Resolving the satellites within the later group requires as high a resolution as possible. In Figure 1, we show this later group of satellites measured at 54 eV and 90 eV photon energy. One clearly sees three components: peak numbered 1 corresponds to a mixture of satellites states with both $2p^5 4s$ and $2p^5 3d$ electronic configurations, peak 2 is mainly due to $2p^5 4s$ satellite states, and peak 3 is assigned to only $2p^5 3d$ satellite states. Peaks 2 and 3 are good references to detect any difference in the energy dependence of the relative intensity of the $\Delta l = 0$ and $\Delta l = 2$ satellites, respectively. At 54 eV, the three components have roughly the same intensity, at 90 eV, the relative intensity of peak 3 has clearly decreased, revealing a significant energy dependence of the $2p^5 3d$ state intensity. The $2p^5 3p$ correlation satellites were all resolved. Detailed results will be presented at the conference and compared to existing photoionization calculations.

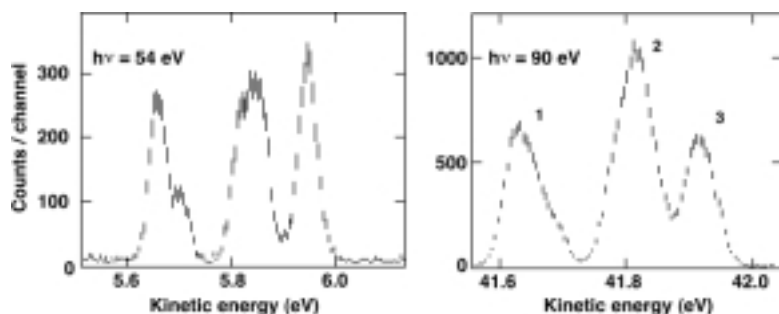


Fig. 1 - Electron spectra showing the intensity of the correlation satellites produced with $\Delta l = 0$ (peak 2, mainly $2p^5 4s$ final ionic states) and with $\Delta l = 2$ (peak 3, $2p^5 3d$ final ionic states) at 54 eV (left panel) and 90 eV (right panel) photon energy, respectively.

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Beat structure in the doubly excited Rydberg states converging to the N=2 threshold of helium

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Doubly excited helium is the prototype system for studying autoionisation phenomena, i.e. the effect of electron correlation. The presence of only two electrons makes it readily accessible for *ab initio* calculations of the parameters describing the autoionisation resonances.

In the present work we investigated the helium Rydberg series converging to the N=2 autoionisation threshold (IP_2) by means of total photoionisation yield measurements. Three Rydberg series are converging to this ionisation threshold, namely the principle ($2, 0_n$) and the secondary series ($2, 1_n$) and ($2, -1_n$). With a resolving power of 90 000 a hitherto unresolved beat structure in the series was observed at very high excitation levels.

Figure 1 gives an enlarged view of the region just below the N=2 ionization threshold. The amplitudes of the autoionisation profiles decrease continuously up to a minimum value at $n = 26$ as already observed in experiments with lower energy resolution [1]. But with the highest currently available energy resolution, an increase of the amplitudes above this profile with a maximum value at the ($2, 0_{29}$) line is observed. For $n > 29$, the amplitude is again decreasing. The beat can be explained by a mixing of two series converging to different ionisation thresholds and having an energy spacing corresponding to the energy split between the $2p_{1/2}$ and $2p_{3/2}$ level of singly ionised helium. This indicates that the electron interaction at high excitation levels can be described within the jj-coupling scheme of two electrons.

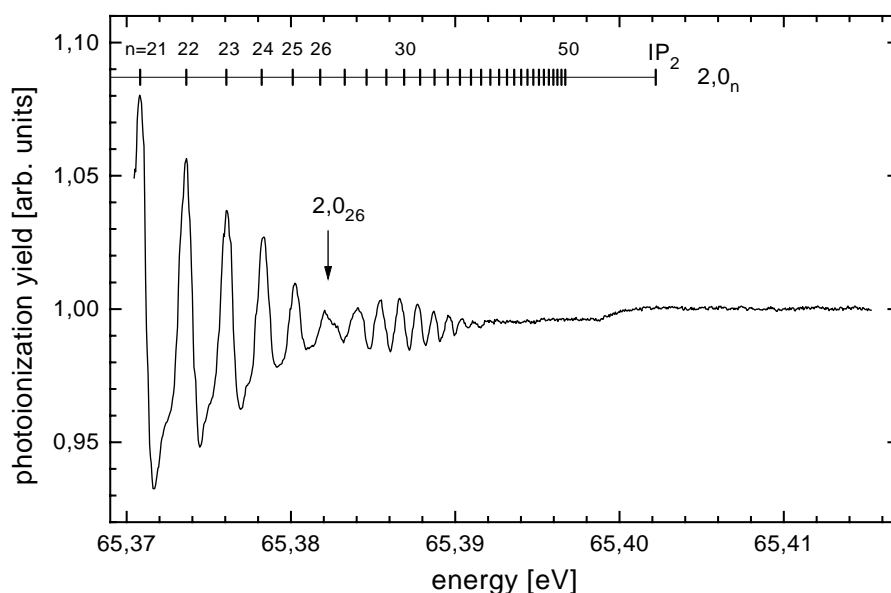


Figure 1: Near threshold region of the N=2 Rydberg series. Between the profiles ($2, 0_{26}$) and ($2, 0_{34}$) a beat structure is observed. The arrow indicates the 26th profile of the ($2, 0_n$) series, where the minimum in the amplitudes occurs. IP_2 denotes the ionization limit.

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NUCLEAR MOTION EFFECTS OBSERVED IN PHOTOELECTRON SPECTRA OF HCL AND DCL MOLECULES

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The HCl inner-valence photoelectron band at 26 eV binding energy has been recorded with a photon energy of 64 eV at high resolution. Discrete peaks arising from at least two separate vibrational progressions are superimposed on the broad continuum. Fano profiles are visible in one of the progressions. This indicates interference between superimposed electronic states. In the isotopic DCl molecular spectrum the discrete lines are much less pronounced. The difference between HCl and DCl is due to dissociation dynamics[1], where non-adiabatic, non-avoided crossing behavior is more pronounced for the lighter HCl molecule. A theoretical treatment of the systems, with simulated spectra based upon the potential curves [2] is also presented.

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Core excitation and ionic fragmentation of aromatic molecules

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C $1s \rightarrow \pi^*$ resonant excitation of benzene yields a core-excited state in which the core hole is localised on a single carbon atom and the aromaticity is lost [1]. This symmetry lowering is accompanied by a rehybridisation of the bonding orbitals of the excited carbon atom, loss of planarity and the excitation of both symmetric and asymmetric vibrational modes. In the case of aromatic molecules of lower symmetry, such as pyridine and toluene, resonant core-excitation can in principal be performed selectively at each of the chemically inequivalent carbon centres, given sufficiently large chemical shifts in the C $1s$ energy levels between inequivalent sites and a sufficiently narrow photon bandwidth. The resulting core-excited states might be expected to have differing vibrational structure depending upon the location of the core-excited atom with respect to that of the heteroatom or the substitution site. In all cases, the core-excited state is short lived; electronic relaxation typically results in multiple ionisation and molecular fragmentation.

Results will be presented of studies of the core excitation spectroscopy and subsequent photofragmentation of a number of aromatic molecules, performed with high resolution using synchrotron radiation and ion time-of-flight mass spectrometry. In particular, the vibrational structure of the C $1s \rightarrow \pi^*$ transitions of benzene, toluene and pyridine, shown in Figure 1, will be discussed and contrasted. The ionic fragmentation processes occurring in these molecules following selective core excitation will be examined as a function both of core-hole position and of vibrational excitation.

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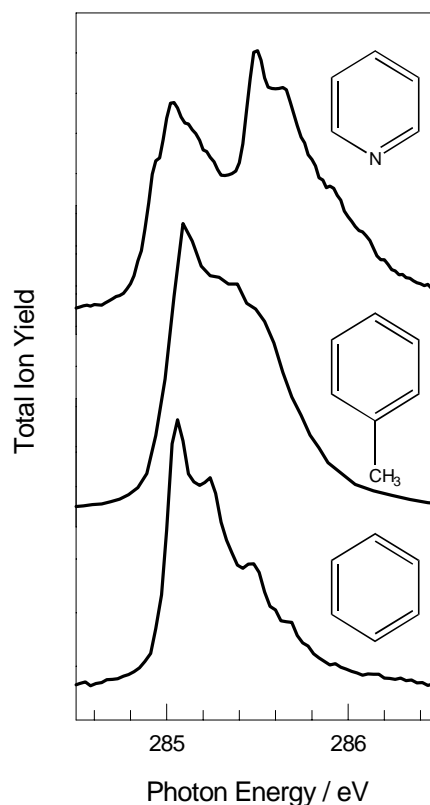


Figure 1. C $1s \rightarrow \pi^*$ total ion yield spectra of pyridine (top), toluene (middle) and benzene (bottom).

NUCLEAR MOTION EFFECTS AS OBSERVED IN THE RESONANT AUGER DECAY TO THE $X^2\Pi$ ELECTRONIC GROUND STATE OF N_2O^+

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High-resolution Auger spectroscopy applied under resonant Auger Raman (**RAR**) conditions is shown to be a powerful tool for characterizing complex potential energy surfaces in core-excited systems. Using the example of $N\ 1s^{-1} \rightarrow \pi^*$ resonant Auger transition in nitrous oxide we emphasize the interplay between the nuclear motion and the electronic decay. We show how the choice of the excitation energy allows selection of core-excited species of different geometries [1,2]. The nuclear dynamics of these species are mapped by measuring the resonant Auger decay spectra. In addition to the changes in vibrational structure observed for the resonant Auger decay spectra, a strong influence of the nuclear motion on the electronic decay is revealed inducing the so-called “dynamical Auger emission”. The experiments have been carried-out at the undulator beamline I411 at the Swedish synchrotron radiation facility Max-Lab in Lund. The experimental results are supported by *ab-initio* quantum chemical calculations restricted to a linear geometry of the core excited state (Figure 1).

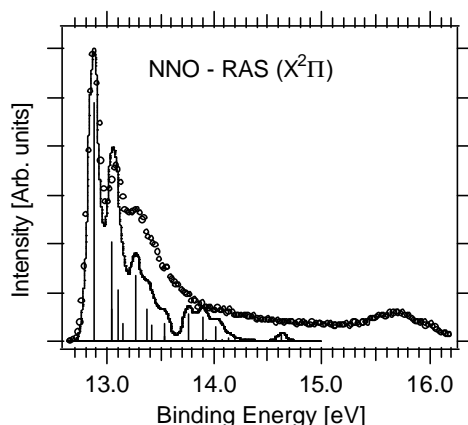


Figure 1: Comparison between *ab-initio* calculations (bars and continuous line) and the experimental resonant Auger decay spectrum (empty circles) of the $X^2\Pi$ electronic state of N_2O measured on the top of the π^* resonance: $h\nu = 401.3$ eV.

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Hot-electron dynamics in mass-selected transition metal clusters probed by femtosecond pump-probe photoelectron spectroscopy

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Clusters in the gas phase are confined systems ideally suited to follow the internal energy dissipation from a non-thermally excited state into the thermal equilibrium. Of emerging interest is the dynamics of excited electrons in a non-equilibrium state, which is created when an electron is photoexcited by an ultrashort light pulse. Here we show by time-resolved photoelectron spectroscopy that electron relaxation processes are efficient energy dissipation channels not only in bulk metals but also in extremely small transition metal clusters [1]. An analysis of the time-resolved two-photon photoemission spectra of optically excited small Ni, Pd, Pt- and metal-carbonyl clusters reveal effective electron relaxation times of less than 100 fs for electrons excited below the vacuum threshold ($h\nu_{\text{pump}}=1.5$ eV). A comparative series of pump-probe spectra of different Pd-clusters demonstrates that the relaxation times vary with the cluster size. This is attributed to the partial density of states of small clusters as deduced from the resonant two-photon photoemission spectra of Pd₃₋₇. In comparison to simple metal clusters, e.g. Ag_n, and Na_n, the bulk-like inelastic scattering processes in open d-shell transition metal clusters are attributed to the larger electronic level density caused by both the small d-bandwidth at the Fermi level and the larger number of valence electrons. Furthermore, statistical evaporation of CO-ligands has been observed as alternative energy relaxation channel in metal-carbonyl clusters. While Pt₂(CO)₅⁻ reveals thermal desorption of a single CO ligand reaching up to the nanosecond regime, Au₂(CO)⁻ desorbs the CO-ligand within some hundreds of femtoseconds. The reason for the high desorption rate in Au₂(CO)⁻ is attributed to the much smaller CO-desorption barrier and the smaller number of vibrational degrees of freedom..

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The electronic structure of supported endohedrally doped fullerenes

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We have investigated the electronic structure of endohedrally doped fullerenes which have been deposited onto a substrate from a mass-selected ion beam [1]. The valence orbitals of endohedrally doped C_{60} can be explained by those of pristine C_{60} , taking a charge transfer and a Jahn-Teller effect into account. The band gap depends on the kind of encapsulated atom, as shown by scanning tunneling spectroscopy. Semiconductor-like and metal-like densities of states have been observed for $Ce@C_{60}$ and $La@C_{60}$, respectively. The core level region exhibits a shift to higher binding energies with respect to the bulk due to metal-to-cage charge transfer processes, as demonstrated by X-ray photoelectron spectroscopy in the case of Ce 3d in $Ce@C_{60}$.

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EVIDENCES OF LOCALIZATION EFFECT AFTER S 1s EXCITATION AND AUGER DECAY IN THE SO₂ AND CS₂ MOLECULES

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We present the measured electron-multi-ion coincidence spectra after photoexcitation of the SO₂ and CS₂ molecules around the S1s edge. A procedure for complete determination of all set of ions formed is described. The dissociation channels and its behavior with the photon energy of these molecules are presented in comparison with the Total Ion Yield (TIY). We observed a charge distribution preferentially of asymmetric form with higher charge in the excitation atom for SO₂ molecule, see Fig.1. In CS₂, similar asymmetric distribution was observed. Furthermore, above S 1s first resonance, the channel with an even charge distribution between the two oxygen in SO₂ in the most abundant. In CS₂ it is not, in it, one of the Sulfur atoms is core ionized. Auger cascade after the 1s core hole creation leading to 2p double hole states need to be taken in to account to explain the observed memory effects. The time scale of the nuclear motion and decay is taken into account to explain the competition between intra-atomic cascade Auger leading to asymmetric charge distribution and Coulomb explosion giving rise to symmetric charge distribution in CS₂. Recombination forming an O₂ ion was found for SO₂

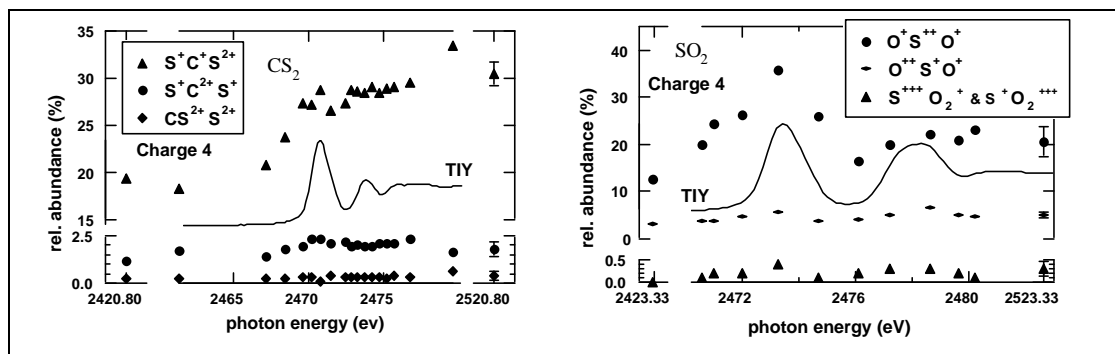


Figure 1: Relative abundance of selected dissociation channels with total ionic charge 4. The total ion yield (TIY) is also shown.

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EVIDENCE AGAINST ATOMIC-LIKE RESONANT AUGER DECAY IN N₂ DOUBLY- EXCITED CORE STATES BY HIGH-RESOLUTION EXPERIMENTS

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Resonant Auger spectra following the decay of doubly-excited core states in N₂ in the range 409-411 eV have previously been assigned to “atomic” lines indicating ultrafast dissociation. Using high-resolution synchrotron radiation electron spectroscopy from the MAX II facility in Sweden we have remeasured the resonant Auger spectrum of N₂ in the vicinity of the N 1s threshold. Contrary to earlier studies, we find vibrational progressions that can be associated to the final C ²Σ_u⁺ and 2 ²Π_g states in N₂⁺. We conclude that the decay is entirely leading to molecular final states.

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Dissociative photoionization of ethylene molecules and clusters in a supersonic molecular beam

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The photoionization and photodissociation cross-sections of ethylene monomers and clusters have been measured in the 20-70 eV photon energy range at the Gas Phase Photoemission Beamline, ELETTRA. Our experimental apparatus is a supersonic beam source coupled to a quadrupole mass spectrometer, that we have specifically developed for the Gas Phase Photoemission Beamline for photoionization studies on atomic and molecular clusters.

In the case of the ethylene monomer the measurement of the branching ratios for the different dissociation channels has allowed us to extend previous synchrotron radiation studies [1], whereas the data on ethylene clusters complete and extend previous investigations carried out using a H₂ lamp and TOF mass spectroscopy [2]. The main fragmentation channels characterizing our spectra correspond to C_{2n}H_{4n}⁺ and C_{2n-1}H_{4n-3}⁺ ions, the latter obtained from the cluster ion by loss of a neutral CH₃ fragment.

Further data on possible correlation between patterns of photofragmentation of the cluster ions and the cross-section for reaction of the ethylene ion with its neutral parent will also be presented.

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THIOPHENE PHOTOELECTRON SPECTRA IN THE GAS PHASE

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The C 1s and S 2p photoelectron spectra of thiophene were investigated with a total instrumental resolution of around 60 meV and 30 meV, respectively. The experiments were performed at the third generation synchrotron radiation facility MAX II in Sweden, at BL I411. The spectra were also theoretically modelled with the Frank-Condon factors calculated using molecular geometries, vibrational frequencies and normal modes for neutral and excited states obtained analogously as described in reference [1].

In the C 1s XP spectrum, two chemically shifted carbon lines (split by 300 meV) are observed, each with a vibrational progression. The S 2p XPS is more complicated due to the molecular-field splitting (MFS) of the S 2p_{3/2} line. Analysis of the spectra results in a value of 99 meV for the MFS, i.e. of the same size as the main vibrational spacing. The MFS has also been calculated using second-order Møller-Plesset perturbation theory and large atomic basis sets. The computed splitting, 93 meV, confirms the value obtained from fitting the experimental spectrum.

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PHOTOIONIZATION OF ATOMIC SCANDIUM

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We are in the process of recalculating the partial cross sections corresponding to the photoionization of 3p, 3d and 4s electrons of the scandium atom in the $[\text{Ne}]3s^23p^63d4s^2$ ground state using our MCHF-enhanced MBPT methodology. In our previous calculations¹ we did not explicitly include photoionization with excitation channels; two-electron transitions that leave the Sc^+ ion in a $[\text{Ne}]3s^23p^63d^2$ state. The threshold energies of these photoionization with excitation channels are nearly degenerate with the 3d and 4s single photoionization thresholds. The calculated threshold energies for the 4s and 3d single photoionization channels are listed in Table I and for the photoionization with excitation channels in Table II.

Table I: Threshold energies for single-electron excitation channels

Ionic Core	$[\text{Ar}]3d4s(^1D)$	$[\text{Ar}]3d4s(^3D)$	$[\text{Ar}]3d4s(^1S)$
Energy (au)	0.2443245	0.2244494	0.26785456

Table II: Threshold energies for two-electron excitation channels

Ionic Core	$[\text{Ar}]3d^2(^1S)$	$[\text{Ar}]3d^2(^1D)$	$[\text{Ar}]3d^2(^1G)$	$[\text{Ar}]3d^2(^3P)$	$[\text{Ar}]3d^2(^3F)$
Energy (au)	0.3717778	0.2993129	0.2985242	0.2863842	0.2713485

We expected markedly different behaviour from our previous calculation,¹ particularly for the 3d partial cross section around its threshold, and our preliminary results indicate that this is so. This region is now dominated by the two-electron resonances corresponding to the $\{3p^63d^2(^1S, ^1D, ^1G, ^3F)\}np(nf)(^2P, ^2D, ^2F)$ autoionizing doubly excited configurations. We are in the processes of calculating the region where the autoionization of the $3p^53d^24s^2(^2P, ^2D, ^2F)$ singly excited resonance configurations play a dominant role. We have obtained partial results for channels with 2F final coupling, and the results indicate an increase in the widths of these resonances because the various $3d^24s^2$ excitations now have other channels to decay into that were omitted in the previous calculation.

This work was supported by NASA and NSF.

Computing grant from Auburn University is gratefully acknowledged.

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Vacuum–UV Absorption Spectrum of Laser Produced Rubidium and Strontium Plasmas

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The Dual Laser Plasma (DLP) photoabsorption technique has been used to measure the time and space resolved VUV photoabsorption spectra of laser produced rubidium and strontium plasmas. In this technique a high power laser is focussed onto the material under investigation (here rubidium and strontium) and an absorbing plasma is formed. After an adjustable time delay a second laser pulse is fired onto a high atomic number target (which is tungsten here) which gives rise to a VUV continuum emitting plasma source used to back–light the absorbing plasma [1].

Data on inner shell transitions are relevant not only for research in atomic structure and dynamics but also for applications in astrophysical, fusion, analytical and materials research. The present work on inner–shell transitions in ions of the Kr isoelectronic sequence follows earlier work on the Ar sequence [2]. We are specifically interested here in excitation of the 3d and 4s subshells of Rb⁺ and Sr²⁺. The 3d–photoabsorption spectra of the Sr isonuclear sequence has already been studied [3] while the corresponding data on the Rb II spectrum are new. We compare these particular data with Hartree–Fock calculations. We will also present the 4s–photoabsorption spectra which can be compared with recent many–body calculations.

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K-Shell Photodetachment of Li⁻ : Experiment and theory

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An experimental K-shell photodetachment/photoionization study of Li⁻ giving rise to doubly photoionized Li⁺ ions has been carried out at the Advanced Light Source, using a collinear photon-ion beam apparatus. The experiment reveals dramatic structure, differing substantially both qualitatively and quantitatively from the corresponding processes in neutral atoms and positive ions, as predicted by our enhanced R-matrix calculation. The experimental/theoretical comparison shows good agreement over some of the photon energy range, and also reveals some puzzling discrepancies.

SYNCHROTRON RADIATION PHOTOEMISSION STUDY OF SOLID PHASE TRANSITION METAL COORDINATION COMPOUNDS

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Core-levels photoemission spectroscopy has been intensively used to investigate Transition Metal Coordination Compounds (TMCC) [1]. Also in this field, in the last 15 years Synchrotron Radiation has allowed much more resolved spectra than traditional X-Rays sources. However its application has been limited to gas phase TMCC samples [2], due to the insulating nature of this kind of molecules, which causes dramatic broadening and shifting of the peaks in solid phase samples. Unfortunately, only a very small number of TMCC can be evaporated without thermal decomposition, thus preventing such application to important fields like bioinorganic chemistry and homogeneous catalysis. High resolution XPS of solid phase TMCC would provide a powerful tool to correlate chemical behaviour with bonding abilities and electron densities.

In order to fully exploit the advantages of such technique, we have searched for an optimal sample preparation, suitable to minimize the differential charging effects. The results obtained with the model compound $W(CO)_4(dppe)$ ($dppe=1,2$ -bis(diphenylphosphino)ethane) show that the best method is by spin-coating a solution of the compound on a conducting support. Then we have compared the spectra obtained by that way with those acquired on samples prepared by more traditional techniques or by evaporating the compound in vacuum on a clean Gold foil. Figure 1 shows the spectra taken at VUV beam-line at Elettra: spectra from traditional techniques (brushing or dipping) are absolutely unacceptable, whereas by optimizing the solvent and the spin-coating parameters the core-levels peaks become narrow enough (FWHM~0.65 eV) to be comparable with the peaks obtained by sample evaporation (FWHM~0.42 eV) and with no significant difference in the chemical shift.

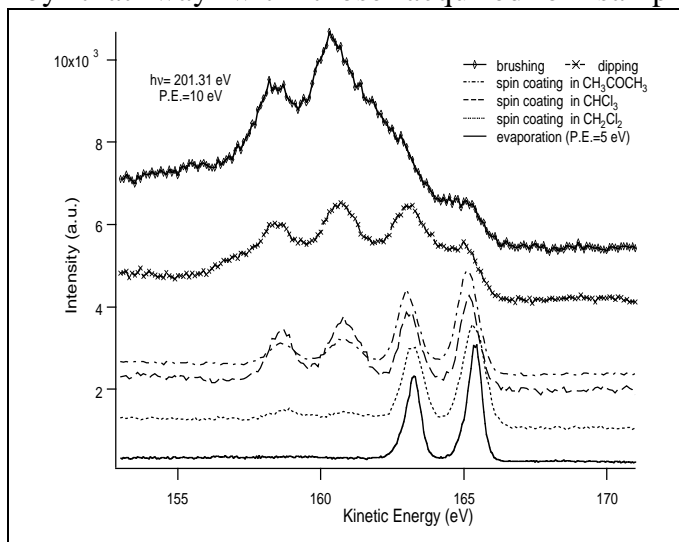


Figure 1: W 4f XPS spectra of $W(CO)_4(dppe)$.

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