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A PROGRESS REPORT

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ULTRA-SOFT X-RAY EMISSION SPECTROSCOPY A PROGRESS REPORT

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Abstract.

A review is presented on recent developments in ultra-soft x-ray emission spectroscopy. Especially, instrumental developments related to high resolution studies of free molecules and to the use of synchrotron radiation are discussed. The most recent results from three different applications of ultra-soft x-ray emission spectroscopy are presented: electron excited spectra of free molecules, monochromatized synchrotron radiation excited spectra of solids and photon emission following charge transfer in slow ion-atom collisions.

Introduction.

Soft x-ray emission originating in transitions between valence states and core states is of considerable interest for studies of the electronic structure of matter. The binding energy separation of the core states in different atomic species makes soft x-ray spectroscopy a chemically selective method, and since the core states are localized the method is able to probe the local electronic structure. Furthermore, the electric dipole nature of the x-ray transitions allows the angular momentum components of the valence states to be separated. For molecules the selectivity of the soft x-ray transitions is particularly useful in connection with the MO-LCAO description of the molecular orbitals. For solids, on the other hand, the total density of states function (DOS) can be resolved in partial components (PDOS).
In the ultra-soft range (below 1keV) emission spectroscopy (USX) has been pursued for the study of free molecules using different means for excitation and wavelength dispersion. High resolution has been achieved by using grazing incidence technique and bright electron excited sources. In low resolution work it has been possible to use photon excitation by means of x-ray tubes. In the x-ray range monochromatized synchrotron radiation has been used to excite spectra of free molecules, revealing interesting phenomena related to the excitation dynamics.

Recent developments in grazing incidence instrumentation and in synchrotron radiation sources has opened up the possibility of using narrow band-pass photon excitation for high resolution ultra-soft x-ray emission spectroscopy. The present paper reviews the first results obtained in this new field. It also discusses briefly the most recent progress in electron excited molecular USX spectroscopy. Finally, the application of high performance grazing incidence instrumentation to charge transfer ion-atom collision experiments is discussed and new results are presented.

Ultra-soft x-ray emission spectra of free molecules.

The MO-LCAO concept (molecular orbitals as linear combinations of atomic orbitals) is particularly useful for interpretation of USX spectra of molecules. Ultra-soft x-ray transitions connect localized inner holes with outer delocalized molecular orbitals by electric dipole interaction. In a one-center approximation only the dipole allowed components of the final state molecular orbital contribute to the x-ray intensity. For symmetric molecules this condition manifests itself as strict selection rules, and in less symmetric molecules x-ray band intensities reflect molecular orbital composition. A number of small molecules (up to the size of aminobenzene) have been studied in high resolution ultra-soft x-ray emission (see reviews and ). Comparisons have been made with theoretical spectra based on intensity models of various degree of sofistication. In particular, the validity of the one-center model has been investigated in order to study its applicability for larger molecules where ab initio methods are not feasible.

The local electronic structure of simple alcohols has been the subject of a recent investigation. Knowledge about orbital composition is valuable for the understanding of bonding mechanisms acting in adsorption on metal surfaces. One question of particular interest is the role of the oxygen 2p lone pair orbital in adsorption processes. Fig.1 shows the oxygen K emission spectra of methanol in comparison with the x-ray spectrum of water. One observes similar spectral features in the two spectra, suggesting that there is a OH x-ray fingerprint not being destroyed when substituting a methyl...
Fig. 1. Oxygen K emission spectra of gas phase methanol and water. Bars indicate one-center intensities.

The attainable resolution in USX spectra of molecules is comparable with the natural lifetime width of the inner vacancy state of the x-ray transitions (0.1 eV). Hence core state lifetimes can be determined from the measured line widths and fine structure due to vibrational excitations can be studied. Vibrational excitations accompanying inner excitations can be considerable due to the relaxation of the outer electrons and manifest...
themselves in the fine structure of the x-ray bands. For instance, a dramatic change in the equilibrium bond length is observed when ionizing a C1s electron in carbon monoxide, while a slight lengthening of the bond is observed when an oxygen core electron is removed /13/. In the case of carbon dioxide the removal of a C1s electron causes a less dramatic decrease in bond length while oxygen core ionization leads to a substantial displacement of the center atom, thereby breaking the symmetry of the molecule /14/.

The interpretation of USX vibrational fine structure in terms of Franck-Condon overlaps is quite successful. Frank-Condon fits to observed spectra yield information about the potential energy surfaces of the core states and in particular changes in equilibrium bond lengths and geometries upon core excitation and deexcitation /12/. In the x-ray emission spectrum of gaseous acetylene the 1Π_u band exhibits well resolved vibrational fine structure, see fig.3. Interpretation is made in terms of multi-dimensional Franck-Condon overlap calculations of core ionization and x-ray deexcitation, and the calculated spectrum is also shown in the figure for comparison /15/.

![Fig.3](image.png)

Fig.3. X-ray emission spectrum of C_2H_2, 1Π_u band. The theoretical spectrum shown to the right is based on a multi-dimensional Franck-Condon calculation.

The finite lifetime of the inner vacancy initial state of the x-ray transitions imposes a limitation to the validity of the Franck-Condon picture. The effect of this limitation is observed in the C K emission spectrum of carbon monoxide /13/. In order to attain full agreement between theory and experiment the phase of the core state wavefunction has to be considered,
Satellite lines are frequently appearing in molecular soft x-ray spectra, which are excited with considerable excess energy. A great deal of satellite structure can be rationalized in terms of multiple ionization and excitation upon inner hole formation while, in other instances, rearrangement processes in the x-ray decay are responsible. In some cases detailed investigations of the satellite spectra have been carried out based on CI and MC-SCF calculations of transition energies. Also, models for simple derivation of satellite energies have been put forward.

Developments in ultra-soft x-ray spectroscopy instrumentation.

The high brightness of the x-ray source required to allow high resolution grazing incidence instruments to be used for studies of free molecules has excluded other means of excitation than electron impact. For solid samples discrete x-ray sources, bremsstrahlung, and broad band synchrotron radiation has been used. The general problem of sample decomposition encountered when using electron impact excitation is in practice eliminated in gas phase studies since sample gas can be continuously replenished in a windowless differentially pumped source.

A new electron excited source for x-ray emission studies of gas samples has recently been constructed, see fig.5. It operates with a Pierce type electron gun, provided with an indirect heated LaB₆ cathode. Focussing of the electron beam (typically 100 mA at 10 keV) is made by a magnetic quadrupole doublet lens which also directs the beam through the entrance slit of a sample gas cell where pressures above 10 mbar are maintained. Three stages of differential
pumping separates the gas cell from the electron gun where pressures below $10^{-5}$ mbar are achieved. Also, three-stage differential pumping is employed between the gas cell and the grazing incidence spectrometer to avoid the use of windows. In order to increase the brightness of the source a solenoidal magnetic field is introduced in the excitation region of the gas cell by means of axially symmetric permanent magnets and a soft iron yoke. The electron beam is focussed by being caught by the convergent field which also increases the path length of the electrons, thereby increasing the excitation efficiency.

Along with the construction of the new source for molecular studies a grazing incidence instrument has been constructed which is portable and has high adaptability to different sources /4/. This design allows us to use also sources at other laboratories, in particular synchrotron radiation sources. Recent developments in synchrotron radiation techniques have provided very bright sources and for the first time selectively excited high resolution spectra in the ultra-soft x-ray range are possible.
The new grazing incidence instrument has been designed according to a new concept which allows a large spectral range to be covered, still providing high resolution and luminosity. In order to satisfy the requirements of large spectral range and high resolution several gratings are used. The gratings are mounted fixed adjacent to each other on a precision ground reference block. This arrangement allows the spectrometer to be given a design which easily adapts to different sources since it dispenses with elaborate mechanisms for change of grating, see fig.6. Instead, selection of grating in use is made by operating a movable aperture between the gratings and the entrance slit so that the appropriate grating is illuminated. The fixed grating arrangement allows in particular the incidence angles to be chosen to match the wavelength regions covered by the different gratings.

Radii of curvature of the gratings, as well as groove densities, may be different which facilitates the accomplishment of optimum performance over the entire spectral region. Obviously, there will be as many focal curves as there are gratings since each grating together with the common entrance...
slit and the (properly positioned) detector forms a Rowland instrument. The 
detector can be positioned at any point on the different focal curves by 
means of accurate translation stages, which are driven by computer 
controlled stepper motors. In particular, the detector can be positioned at 
off-Rowland positions which is of importance when striving for maximum 
efficiency at moderate resolution. The reason for this is that the spherical 
aberration moves the best focus away from the Rowland circle when the 
grating width is increased.

Detection is made by a large (40 mm) CsI coated multichannel plate (MCP) 
sensor provided with two-dimensional read-out based on resistive anode 
technique /24/. Two-dimensional read-out is necessary in order not to 
impair the resolution due to the curvature of the spectral lines and to 
account for image distorsion in the detector read-out. The efficiency of the 
MCP is considerably higher at near normal incidence than at grazing angles. 
Therefore the detector can be rotated to a near normal orientation to be used 
in low resolution-high efficiency mode. In high resolution mode the rotation 
mechanism is used to orient the detector to be tangential to the focal curve. 
A considerable improvement of the efficiency at grazing angles is 
accomplished by using a repelling electrode in front of the MCP. It consists 
of a set of 50 μm wires running parallel with incoming radiation 2 mm above 
the detector surface and is given a negative potential of several hundred 
volts. The CsI coating is essential for the efficiency /25/, although it 
introduces the inconvenience of constantly keeping the detector in vacuum or 
in dry air due to the hygroscopic properties of this coating material.

The spectrometer design permits spherical gratings to be used without large 
astigmatic losses in sensitivity. The large imaging detector is instrumental 
for this achievement which permits high sensitivity and high resolution to be 
atained simultaneously. The sensitivity depends on wavelength and 
resolution selected but as a typical example the high resolution (0.07 eV at 
280 eV) sensitivity is 10⁻⁸. This means that 10⁸ photons from the sample 
are required to yield one detected count (spot size on the sample is assumed 
to be 0.2 x 5mm²). In low resolution mode (0.6 eV at 280 eV) the sensitivity 
is 4·10⁻⁷. Since typical yields for soft x-ray fluorescence are in the order of 
10⁻⁴ we thus require a flux of exciting particles/photons per second of 10¹¹ 
to 10¹³ on the sample. This is easily achieved in a fine focusing electron 
beam and, as shown below, it can also be attained in a beam of 
monochromatized photons at a storage ring.

The resolution of the instrument is set by the spatial resolution of the 
detector, which is about 60 μm in the direction of dispersion. The 
corresponding entrance slit sizes are in the 5-10 μm range. Fig.7 shows the 
ultimate resolution for a configuration of two 5 m gratings and one 3 m

The use of synchrotron radiation for excitation of soft x-ray spectra has several advantages. Synchrotron radiation sources are very bright compared to other sources and, as will be demonstrated below, they even allow primary monochromators to be used to obtain selectivity in the excitation. By using narrow band-pass excitation overlaying satellite lines can be isolated and accidental occurrence of irrelevant transitions (like inner-core transitions and higher order spectra) eliminated. Also, threshold phenomena and resonant behaviour can be studied in detail. Another aspect of importance is that of radiation damage \cite{26}.

Chemically fragile samples are more likely to survive the dose required in exposure to monochromatized exciting photons than in broad band excitation.

The first series of experiments in ultra-soft x-ray emission using
monochromatized synchrotron radiation were carried out recently at the synchrotron radiation laboratory (HASYLAB) at DESY in Hamburg. The experiment was set up at the FLIPPER I multipole wiggler beam-line. The FLIPPER I monochromator employs a plane grating for dispersion and a parabolic mirror for focussing on the exit slit. A set of premirrors at various incidence angles are available to suppress higher order radiation. Measured output lies in the $10^{12}$-$10^{13}$ s$^{-1}$ range at resolutions between 0.5 eV and 10 eV in the 20 eV to 1 keV photon energy range /5/. As discussed above this photon flux is of the required magnitude to allow fluorescence spectra to be recorded in high resolution. In fig.8 is shown a photograph of the new grazing incidence instrument attached to the experiment chamber at the FLIPPER I station.

In the following we present briefly some of the results obtained in the first experiments. Reference to papers presenting more thorough discussions are given passing the different subjects.

In the ultra-soft x-ray emission spectrum of TiN part of the Ti L emission (3s-2p) overlaps the N K emission. This has presented problems for x-ray band structure investigations of this compound since the separation of the Ti L spectrum requires the excitation energy to lie between the thresholds for N1s and Ti2p, a restriction that has not been met in previous work. Attempts to overcome this difficulty have been made by subtracting the known 3s-2p
We have recorded the N K emission spectrum of TiN using monochromatized synchrotron radiation for excitation, thereby obtaining the pure spectrum. In addition, by tuning the excitation energy down to near threshold we can remove satellite structure appearing at excess energy excitation to obtain the undistorted band spectrum mapping the N2p contribution to the valence band, see fig.9a. The spectrum has been aligned to the Fermi energy using XPS binding energy data.

In fig.9b is shown the Ti L\textsubscript{III} emission spectrum obtained by tuning the excitation energy to 458 eV, i.e. below the L\textsubscript{II} threshold, and aligned by means of XPS data. Comparing the N K and Ti L\textsubscript{III} spectra gives a complementary picture of the valence band. The results support band structure calculations describing the outermost band as mainly Ti3d and the 5 eV band as N2p with a significant contribution of titanium d electrons /29/.

Fig.9c shows the difference between Ti L emission spectra recorded at energies well above and below the L\textsubscript{II} threshold. The resulting spectrum, which presumably would show the L\textsubscript{II} emission, does not resemble the L\textsubscript{III} spectrum as expected. Also, the intensity of the difference spectrum is much too high to be in concordance with the L\textsubscript{II} Coster-Kronig depopulation rate /30/. In order to explain these observations we turn to fig.10, which shows a series of Ti spectra recorded at various excitation energies. We see that the spectrum reveals a resonant behaviour when the excitation energy passes through the 460-470 eV region, with a maximum intensity of the 460 eV line at 465 eV excitation energy. We explain the observed resonance as the decay of an atomic like L\textsubscript{III}-3d state populated via Coster-Kronig decay of an L\textsubscript{II}-3d
state. The absence of the normal Ti L\textsubscript{II} spectrum is explained by the strong Coster-Kronig decay of the L\textsubscript{II} vacancy. A more detailed discussion of the present results can be found in ref./31/.

The usability of selective excitation for soft x-ray spectroscopy is also demonstrated in the L emission spectrum of Cu, shown in fig.11/32/. The spectrum excited with 970 eV photons shows two bands corresponding to a band electron filling a 2p\textsubscript{1/2} or 2p\textsubscript{3/2} vacancy, respectively.

Fig.10. Titanium L emission spectra of TiN excited at various photon excitation energies.

Fig.11. Cu L\textsubscript{II,III} emission spectra of copper metal excited at different photon excitation energies.
Coster-Kronig decay of L_{\Pi} holes and shake-off processes in L_{\Pi\Pi} hole formation are expected to give rise to satellites superimposed on the L_{\Pi\Pi} band. Exciting the emission below the L_{\Pi} threshold and near the L_{\Pi\Pi} threshold removes the L_{\Pi} line and the satellites and it allows the clean L_{\Pi\Pi} bandspectrum to appear. The relative intensities of the L_{\Pi} and L_{\Pi\Pi} lines and the satellite contribution then yield information about the strengths of the non-radiative decay channels and about the shake-off probability.

In an investigation of the copper L and oxygen K emission spectra of high T_{C} superconductors the same technique as for copper metal was employed. Spectra were recorded at excess excitation energies and near thresholds allowing the satellite structure to be separated from the diagram spectra. Fig.12 shows the Cu L_{\Pi\Pi} and O K emission spectra of YBa_{2}Cu_{3}O_{7} recorded at near threshold energies and aligned to the Fermi level by means of photoemission and x-ray absorption data. The near threshold excited spectra are supposedly free from satellites and thus map the partial density of states of Cu3d and O2p character, respectively. Apart from enabling the decomposition of the total DOS the present method provides another important quality in that it probes the electronic structure of the bulk of the material. This is particularly important for the ceramic superconductors which are known to change surface composition in vacuum.

![Fig.12. Copper L_{\Pi\Pi} and oxygen K emission spectra of a high T_{C} superconductor.](image)

Ultra-soft x-ray emission in charge transfer collisions.

Laboratory studies of the interactions of highly charged ions play an important role for the understanding of plasmas. While hot plasmas like the solar corona is dominated by electron impact excitation certain cold plasmas in space may critically depend on charge transfer to radiating excited states of highly charged ions. In fusion plasmas both types of processes can occur. Diagnosis of plasmas is commonly made by studying the photon emission spectrum to obtain level population rates which reflect the dynamics of the plasma.
In recent experiments we have applied high resolution ultra-soft x-ray emission spectroscopy to the study of charge exchange in slow ion-atom collisions. The work was made at the Minimafios ECR ion source at the LAGrippa-CEA-CNRS facility in Grenoble /35/. A charge specific beam of highly charged ions, produced in the ECR source and purified in a double separator magnet was brought to collide with a target of helium or molecular hydrogen at pressures in the 5-10×10⁻⁵ mbar range. Photon emission in the 20-250 Å region subsequent to electron capture in the collision was recorded using the new portable grazing incidence instrument described above /4/. Systems studied were He-like N⁺, O⁺, F and Ne ions colliding on He and H₂ targets at velocities near 1 a.u. Experiments of this kind have been made previously by several workers, see e.g. /36,37,38/. However, as will be demonstrated below the performance of the new grazing incidence instrument allows spectra to be recorded with considerably higher resolution and quality than before revealing new information.

In fig.13 are shown emission spectra in the 100-200 Å range recorded in collisions between 60keV O⁶⁺ ions and helium.

Fig.13. Photon emission following electron capture in 60 keV O⁶⁺ collisions with helium and molecular hydrogen.
respectively molecular hydrogen. The insets are plotted with enlarged scales to bring out the low intensity lines. Both spectra show a large number of peaks which have not been observed in a pure collision experiment before. The intense peaks, seen already in the non-magnified spectrum, mostly correspond to single capture processes. The difference in the intensity distributions between helium and hydrogen reflects the capture cross section dependence on the target electron binding energy: the less tightly bound hydrogen electrons are more likely to populate n=4 states while the helium 1s electrons are dominantly captured in n=3. We have determined the single capture cross sections from recorded line intensities by correcting for detection efficiency and accounting for branching ratios. The results for He are shown in table 1 together with previous experimental determinations based on measurements partly in other wavelengths and calculated cross sections.

Table 1. Single capture cross sections for 60 keV O\(^{6+}\) on He.

<table>
<thead>
<tr>
<th>State</th>
<th>Present work</th>
<th>Previous exp.</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/37/</td>
<td>/40/</td>
<td>/42/</td>
</tr>
<tr>
<td>3s</td>
<td>0.51</td>
<td>0.36</td>
<td>0.40</td>
</tr>
<tr>
<td>3p</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3d</td>
<td>0.58</td>
<td>0.52</td>
<td>0.56</td>
</tr>
<tr>
<td>4s</td>
<td>0.025</td>
<td>-</td>
<td>0.013</td>
</tr>
<tr>
<td>4p</td>
<td>0.030</td>
<td>0.034</td>
<td>0.026</td>
</tr>
<tr>
<td>4d</td>
<td>0.13</td>
<td>0.17</td>
<td>0.066</td>
</tr>
<tr>
<td>4f</td>
<td>-</td>
<td>0.15</td>
<td>0.073</td>
</tr>
</tbody>
</table>

Single capture to metastable ions are also observed in a number of cases, giving rise to transitions in the quartet system. A few of these lines have been found to correspond to non-core conserving capture, i.e., excitation of the core in the capture process.

A number of lines, observed predominantly in collisions with helium, have been identified as transitions in O\(^{4+}\), indicating double capture processes. Some of the lines correspond to double capture to states involving high quantum numbers, e.g., 2s6f, with very low cross sections for single capture. This is indicative of strong electron correlation in the capture process. Evidence of correlated double electron capture to autoionizing states has been observed in Coster-Kronig spectra, but to our knowledge this is the first observation in photon emission.
Conclusions.

A progress report is given on ultra-soft x-ray spectroscopic studies of molecules and solids. In particular, recent instrumental developments are discussed. For the first time monochromatized synchrotron radiation has been used to excite ultra-soft x-ray emission spectra, recorded in high resolution. This achievement opens up a new source of information in x-ray spectroscopy, and several advantages with the technique are demonstrated by the results presented. The application of high performance grazing incidence technique to the study of charge transfer in ion-atom collisions is also discussed. It is demonstrated that substantial improvements in spectral quality are possible, and new results from charge transfer studies are presented.

Acknowledgement.

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References.

The detector is a custom design version of a detector developed by Surface Sci. Labs., Mout. View, California.