

Workshop Report on
New Directions in Soft X-Ray Photoabsorption

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ABSTRACT

The Workshop Report integrates what was said at the Workshop on New Directions in Soft X-Ray Photoabsorption, which focused on the region from 100 eV to 10 keV. The report clarifies the current state of theory and experiment and identifies the opportunities which new theoretical methods and experimental facilities could be expected to provide. The understanding of photoabsorption (which requires experimental photoabsorption cross section data) is a key to understanding the properties and behavior of atoms, molecules and solids. The Workshop participants were forty-three physicists and quantum chemists, from twenty-four institutions in four countries, all interested in photoabsorption from different perspectives.

Executive Summary

Introduction: Workshop Description

Nancy Kerr Del Grande

L-Division of the Lawrence Livermore National Laboratory hosted a Workshop on New Directions in Soft X-Ray Photoabsorption held at the Asilomar Conference Center in Pacific Grove, California, on April 8-11, 1984. There were forty-three participants representing twenty-four institutions in four countries. About one-fourth of the attendees were members of six LLNL divisions in two departments at LLNL. "L" Division is one of the major experimental physics divisions.

The thrust of the Workshop was to understand total photoabsorption cross sections for isolated neutral atoms, excited atoms and atoms in environments; focusing on the range 100 eV to 10 keV. Related phenomena, such as photoelectron spectroscopy, were included insofar as they elucidated photoabsorption cross sections. The intent of the Workshop was to clarify the current state of theory and experiment and to identify the opportunities which new theoretical methods and experimental facilities could be expected to provide.

The Workshop attracted key people, maintained their enthusiasm, and expanded everyone's horizons. It was timely, extremely interesting and very productive. It put theoretical and experimental activities in good perspective. These were the reactions expressed by many of the participants in letters we received afterward.

The active participants included many of the world's most renowned atomic physicists. Their interest in photoabsorption reflects the fact that it is one of the most basic physical processes. The understanding of photoabsorption (which requires experimental photoabsorption data) is a key to understanding the properties and behavior of atoms, molecules and solids. The rapid growth of x-ray optics (which requires using optical constants to design instrumentation) is likely to expand our horizons in many areas of physics during the next decade. The Workshop brought together a wide cross section of physicists and quantum chemists, experimentalists and theorists, all interested in photoabsorption but from different perspectives.

The efforts of the Program Committee, chaired by Professor Richard Pratt of the University of Pittsburgh, a LLNL consultant, were largely responsible for the well-balanced technical program. The committee included LLNL physicists Nancy Del Grande, Paul Ebert, Arthur Toor, Richard Fortner and James Scofield, LBL Director David Shirley, Professor Walter Johnson from Notre Dame University and Professor John Weaver from the University of Minnesota.

The Program Committee selected the session organizers, who chaired the eight sessions, and the five review panelists who spoke at the last session. The review panel session was taped, transcribed and has been edited by the panelists. An Executive Summary was written to emphasize some of the session highlights. The full-length reports of the panelists were intended to integrate what was said during the sessions. Photocopies of materials used for individual presentations are on file; copies of the materials for any presentation can be made available upon request. Appended to the Workshop Report is the technical program and a list of participants.

The Organization Committee was chaired by Nancy Del Grande and aided by the L-Division Leader, Richard Neifert; the X-Ray Measurements Group Leader who acted as LLNL's host, Hal Mallett; and LLNL's Registrar, Janice Meamber, who worked tirelessly to achieve a pleasant and productive gathering. The goal, to generate interactions at the Workshop that would be a source of stimulation, ideas and direction-setting was achieved. The attendees, all of whom participated actively, made this possible.

Executive Summary

Basic Theory: Capabilities and Prospects

Richard Pratt

In the opening session of the Workshop, Lloyd Armstrong had given an overview of theoretical capabilities and prospects, reviewing the various approaches for the calculation of photoabsorption which have been developed in recent years. Within nonrelativistic dipole approximation the problems are to calculate the initial and final state wave functions. For the initial state of an n -electron atom the traditional techniques are CI (configuration interaction), MCHF (multi-configuration Hartree-Fock), and MBPT (many body perturbation theory). For the final state one has an ionic state of $n-1$ bound electrons together with one continuum electron. In addition to the ionic state one must describe intra-channel and inter-channel interactions involving the continuum electron; of these the intra-channel interactions (involving interaction of states differing only in the energy of the photoelectron) are relatively easy. In the inter-channel case, CI is replaced by a K -matrix approach, MCHF by close coupling. These are "global" approximation schemes. By contrast, R -matrix and related methods divide space into two regions, with a boundary large enough that the continuum wave function can be easily obtained in the outer region, while a complete set of discrete states can be used in the inner region. Now, in fact, it is not true that one need (should) separately calculate initial and final states. MBPT actually looks at the process, not the states, while the newer RPA (random phase approximation) methods calculate initial and final states simultaneously.

The Basic Theory session began with three talks which reviewed the newer theoretical developments in photoabsorption. Walter Johnson discussed RPA and relativistic effects particularly in the context of RRPA (relativistic random phase approximation). Considerable success has been achieved, as for example in Xe. However, at least one significant failure is now known, in the calculation of the asymmetry parameter for ionization from the Xe 5s shell in the 1 - 1.5 a.u. photon energy region. In this situation the relativistic TD-LDA (time-dependent local density approximation) is better, and in fact, in

many cases this theory, which is much simpler, does at least as well as RRPA. Andrew Zangwill reviewed the use of these density functional methods in photoabsorption. Here, as in RPA, one considers the change in electron density which has been induced by the external photon field. The HF starting point includes exact exchange, but no correlations; the LDA starting point approximates exchange but also includes an approximation to correlations. The RTDLDA can be further improved by inclusion of core-hole relaxation. In the third talk Hugh Kelly discussed the interplay between double photoionization and Auger processes.

Five shorter contributions were presented in the basic theory session. Kwok Tseng Cheng discussed shape resonances in inner shell photoionization. Nancy Del Grande compared sub-keV uranium calculations with experiment. One electron theory agrees with experiment above 800 eV but fails below 200 eV; the local-density based RPA methods of Göran Wendin represent a substantial improvement but are not in quantitative agreement. Vojislav Radojevic discussed a multiconfiguration Tamm Dankoff approximation for $5p_{3/2} \rightarrow nd$ autoionizing lines in the $4f \rightarrow \epsilon d$ cross section of Yb. Balazs Rozsnyai discussed inner shell photoionization in heavy elements. James Scofield discussed exchange effects on cross sections due to relaxation. These effects, added to shake excitation effects, gave rise to 20% overall effects in the K-threshold region for Zn. The magnitude and energy range of these corrections is suggestive that such effects will have to be considered in explaining the differences of theory from the measurements of Del Grande and Oliver for the transition elements.

Executive Summary

Effects of Environment on Cross Sections for Molecules and Solids

Ingolf Lindau

The session on the "Effects of Environment on Cross Sections for Molecules and Solids" covered both theoretical and experimental aspects. With reference to other sessions in the workshop, it was pointed out that a comparison between theory and experiment is a difficult task for atoms, and that this difficulty is enhanced for cross sections of levels taking part in the bonding of atoms in molecules and solids.

Two theoretical talks addressed solid state effects in the analysis of EXAFS (Extended X-Ray Absorption Fine Structure) data. John Rehr reported on the impressive progress he has made in understanding and accounting for inelastic scattering processes. And, Robert Albers demonstrated how the near-edge structure in the photoabsorption can be combined with the EXAFS part of the spectrum and yield significantly better insight into both the electronic and structural properties.

Andrew Zangwill reviewed the theoretical understanding of the effect of the solid state environment in so-called resonance photoemission. Resonance photoemission refers to the situation where the onset of the excitation from a deeper lying core level results in the enhancement of the cross section for some other electronic levels, e.g., more shallow core lines or valence levels. Zangwill emphasized that very little has been done theoretically so far. From a spectroscopic point of view, the resonance photoemission technique can be used, as was pointed out by both Zangwill, Weaver, and Lindau, to study mixed valence states on the surface of rare earth metals and compounds. And, Zangwill described a theoretical model of how the solid state environment can account for the 4f valence fluctuations on Sm metal surfaces.

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John Weaver concentrated his talk on the spectroscopic aspects of resonance photoemission. The cross section enhancement can be used in a spectroscopic sense to determine the binding energy position of 4f levels in valence bands and illustrated this in detail for Ce metal, where the position of the 4f level has been a controversial issue for many years. Furthermore, Weaver showed that the details of the cross section enhancement depend on the changes in the sp-d rehybridization when a d-metal is bonded to a semiconductor substrate. Again, the resonance photoemission can be used as a spectroscopic tool to probe the changes in the chemical environment on an atomic scale.

Both Ingolf Lindau and Tom Carlson discussed experiments where the energy dependence of partial photoionization cross sections had been determined for valence levels in solids and molecules with a so-called Cooper minima. The Cooper minimum occurs for wavefunctions with a node and results in a deep minimum in the partial photoionization cross section. Since the magnitude of the cross section changes rapidly over a fairly small energy region, it is convenient to use spectroscopically to monitor the effects of changes in the environment. Ingolf Lindau showed experimental results illustrating the extreme sensitivity of the cross section to changes in the nature of the d-orbitals (d-d overlaps) in transition metals. He also provided evidence that the Cooper minima technique can be used spectroscopically to distinguish between bonding, non-bonding, and anti-bonding d-orbitals in the formation of the Mo-Si interface. This is another example where the solid state environment has pronounced effects on the cross section and where we are lacking a theoretical model/description.

In summary, it was shown that the environment can have very strong effects on the cross section and will affect the absolute values very significantly in certain energy regions. So far, very little has been done theoretically to understand the environment effects from a fundamental point of view. From a spectroscopic point of view, cross section measurements have developed as a sensitive analytical technique to probe subtle changes in the environment.

Executive Summary

Effects of Environment on Cross Sections for Excited States and Ions

A. L. Merts

This meeting presented several interesting and informative papers about new calculational aspects for photon absorption in atoms (ions) over the photon energy range from approximately 0.1 to 10 keV. These talks showed results from calculations such as: linear response calculations by Gary Doolen and David Liberman, photoionization from excited atoms by Tu-Nan Chang, dense plasma parameters and conditions by Richard More, and observations such as: time resolved plasma spectroscopy by Richard Fortner and laser-plasma X-UV sources by David Nagel.

The paper on "Time Resolved Spectroscopy" was informative in that it clearly displayed the measurement capabilities, needs and problems in a real plasma. The paper on plasma X-UV sources pointed out the possibility of using plasma sources for measurements of plasma parameters.

Richard More's talk delineated those plasma parameters which are important in plasma interactions at various temperatures and densities.

Tu-Nan Chang's talk emphasized the necessity of going beyond the simple independent particle model of the atom. This is especially true when exciting any electron other than the outermost electron in an already excited atom (ion).

From a practical point of view for the users, a very important point was a large set of data tables by use of linear density functional calculations presented by Gary Doolen. The photoabsorption cross sections were compared with the available measurements. The disagreement with measurements was found to be worse at the higher energies than for independent particle calculations when compared with measurements. However, as a result of the conference, the linear density functional code was re-examined, and David Liberman found an error in his code. Comparison of the corrected code with experiment have shown about 15% agreement for the worst cases, but more typically about 5% agreement at 1-10 keV for eight elements (i.e., Fe, Ni, Cu, Sn, Ta, Pt, Au and U).

One effect the "LDA" produces, that the independent particle model cannot, is resonance behavior manifested in the neighborhood of the photoionization threshold. The resonances are narrow and strong, but when averaged over a photon distribution, contribute a positive definite contribution to rate coefficients and cannot in general be neglected. If the photon distribution is not essentially flat over the interesting regions, one cannot count on the oscillator sum rule to produce the correct rate coefficients. It is clear that more work is needed in this important area.

Executive Summary

Experimental Capabilities and Prospects

Roger Bartlett and Nancy Kerr Del Grande

Overview talks on the low energy experimental situation for photoabsorption measurements were given by John Weaver and Pierre Dhez during the Workshop's opening session. The special session on experimental capabilities and prospects discussed the systems used for photoabsorption measurements, over the difficult 40 eV to a few keV energy range.

A talk by Walter Trela discussed synchrotron source characteristics and one by Michael Moran discussed transition radiation source properties. Recent grating monochromator design improvements described by Glenn Tirsell are expected to remove the larger than 50% systematic errors from high order harmonics and stray light. These effects may partly account for the factors of 3 to 6 differences between early experiments and recent theory (e.g., uranium at 200-400 eV) discussed in other sessions.

Other speakers were Roman Tatchyn, who discussed using transmission gratings, and Troy Barbee who discussed using multilayers. These unique sample configurations have less sensitivity to surface contamination which plagues optical constant measurements of single thin film foils. Some of the other sample-related problems for thin films were uniformity, pinholes and determining the density.

UHV compatible crystal monochromators, described by Paul Cowan, will work down to about 800 eV, which overlaps the 40-1000 eV range for double grating monochromators described by Glenn Tirsell. The advantages of two-dimensional detectors over this energy region were discussed by Tom Callcott.

Cross section measurements are needed to pin down theory. One would like to have, at the very least, good measurements for a low-Z, high-Z, open-shell, closed-shell system, or whatever is necessary for a good check of theory. One would like to find out where the errors are. Once this is done, and evaluated theory is available, there is no use competing with it. We don't want to

produce 10^4 curves at a synchrotron, when Gary Doolen could produce them on the Cray computer.

Optical constants should be known to a high precision in the soft x-ray range because of the practical need for x-ray optics to design and evaluate systems accurately. An earnest plea emerged in the discussion following the session encouraging openheartedness in reviewing proposals that would allow money to be granted for these measurements to proceed.

A helpful way to debug the artifacts in our cross section measurements, suggested by Pierre Dhez, would be to make comparisons with energy loss spectroscopy measurements described by Chris Brion. It would enable us to understand many, many details, such as resolving the large numerical differences between theory and experiment for uranium.

The emphasis on cross section measurements using synchrotrons during the early 1970's has changed, according to John Weaver and Pierre Dhez. Hardly anyone is pursuing these measurements today, although our needs and our capabilities have increased significantly. The laser-, crystallographic- and defense-oriented scientific communities would greatly benefit from better cross section measurements. They have stronger "unions" and more funding than the atomic physics community.

We now believe that the technical capability exists to measure absolute photoabsorption cross sections in the soft x-ray energy range to an accuracy of 1 to 5%. To do this will require the use of state-of-the-art components throughout the measuring system. It will require careful sample preparation and handling.

Synchrotron sources, coupled with the latest innovation in monochromators and filter systems are the "best" photon sources in the soft x-ray regime at the present time. Two major difficulties have been lack of time on these sources and lack of funding for cross section measurements.

[Editorial comment: As a result of correspondence after the Workshop, we learned that Professor C. Bonnelle plans to undertake some new soft x-ray photoabsorption measurements at LURE before the next Workshop on this subject.]

Executive Summary
Insights from Related Observations

Steve Manson

The photoabsorption cross section can be measured using methods other than photon attenuation. These methods provide an extremely useful check on direct photoabsorption studies. In addition, and perhaps more important, these "related observations" can give information on the cross sections for the individual processes whose sum is the total photoabsorption cross section. This allows a far more meaningful comparison with theory and makes a full assessment of theory possible. Thereby, the specific channels where the theory is good and those where it is inadequate can be elucidated, paving the way for improvements where they are needed.

Photoelectron spectroscopy is one extremely important technique to scrutinize the photoabsorption process. In addition, monitoring the energy loss of fast electrons in coincidence with ejected electrons [(e,2e) spectroscopy] is closely related to the photoabsorption process and is referred to as "photoelectron" spectroscopy. These techniques can also look at photoelectron angular distributions which provide still further information on the absorption process.

When the photoelectron comes from an inner shell, or the ion is left in an excited state, the de-excitation by emission of a photon (fluorescence spectroscopy) or an electron (Auger spectroscopy) can be studied, giving much the same information as photoelectron spectroscopy. These methods have some experimental advantages in that the detector looks at a single photon or electron energy, in each case. In addition, detailed information on the state of the ion can be obtained.

In summary, a number of techniques can be used to monitor the photoabsorption process which provide related and complementary information to direct photoabsorption measurements.

Executive Summary

Efforts at Systematic Assessment and Tabulations

Nancy Kerr Del Grande

This session clearly indicated that the region from 0.1 to a few keV was not so well understood as commonly felt. Unfortunately, there is no activity in this region. Yet, this energy region for photoabsorption is plagued with problems, both experimental and theoretical. On the experimental front there exist very significant discrepancies between experiments from different laboratories. It is important to clear this up. On the theoretical front the interplay of relativistic and many-body effects can give cross sections which differ from the central-field model results by as much as an order of magnitude.

At 1-10 keV it would appear that in most cases we have good theory and experimental measurements that agree. [Editorial comment: High quality measurements were made at 1-10 keV for Fe, Ni, Sn, Ta, Pt, Au, Pb and U with 3% or less overall errors at LLNL]. Apart from near-edge regions, they agreed, typically within 2-5%, with the relativistic Hartree Slater (RHS) calculations by Scofield and the independent particle approximation (IPA) calculations by Liberman.

However, more work is needed to explain why measurements averaged over EXAFS (extended x-ray absorption fine structure) fluctuations are 10% higher than RHS calculations for six elements, Ti-Zn. [Editorial comment: Scofield has calculated exchange and excitations which together increase the RHS calculations ~20%. These effects should vary as $1/Z$, which would make them twice as large for Mg and Al as for Fe. Measurements taken at LLNL for eleven elements, Zr-U, imply that the effect is smaller for high-Z elements.]

John Hubbell has identified a situation where further work is needed to resolve a possible 15% discrepancy for Cu. In this case, differences between measurements from many laboratories and RHS theory are largest at 1-3 keV, above the L-edges for Cu. Measurements were averaged to obtain a "best fit" value for evaluated experimental data in the McMaster tables. These "best

fit" values were higher than the RHS calculations in Scofield's tables, when adjustments were made for scattering. Hubbell noted, also, that at higher energies (above 30 keV), there is a possible discrepancy between experiment and theory for Si. This may relate to the uncertainty of scattering calculations.

Another example of the problems between theoretical data on a fundamental process and observation was given by C. D. Wagner, who discussed attempts to reconcile observed sensitivity factors in photoelectron spectroscopy with basic cross section data, where apparent discrepancies were 10-40%.

[Editorial comment: Caution is warranted when tables of 1-10 keV photoionization cross sections are used, based on evaluations made at LLNL and at NBS which weren't reported at the Workshop. There were some numerical differences as high as 20-50% at energy regions where measurements were sparse or theory was inadequate (e.g., for Fe, Ni, Sn, Ta, Pt, Au, Pb, U). Among the widely used tables (e.g., by McMaster et al.; Veigele; Storm and Israel; Henke et al., Scofield; Biggs and Lighthill; Plechaty et al.) there were four or more different tables used as databases for computer calculations at LLNL, LANL, SNL and NBS.]

The user-community sponsored by the International Union of Crystallography, has a project to remeasure x-ray attenuation coefficients (e.g., C, Cu and Si). They hope to improve over the McMaster tables (co-authored by Del Grande, Mallett and Hubbell). The X-Ray Measurements Group of L-Division is participating in the project, which was described by John Hubbell.

At 10-1000 eV, Eugene McGuire reviewed major differences between synchrotron measurements and Herman Skillman calculations (e.g., for Mg, Cu, Ag, Au). Some differences, mostly below 200 eV, were factors of 2 to 10. Sub-keV tabulations depend almost exclusively on theory (e.g., Veigele, 1973; Henke et al., 1982, using theory with empirical adjustments). As we saw for one element, U, empirical adjustments can range from a few percent at 800-1000 eV to an order of magnitude below 200 eV. Yet, the measurements were fraught with errors (e.g., from poor monochromators, samples with surface oxides, unfiltered harmonic signals, stray light). And the theories differed by factors of

2 to 10 at the lower energies (based on a comparison of LRA and IPA theories by Gary Doolen instigated by interested workshop members).

Our present databases suffer from credibility. Shape resonances and delayed maxima are not well measured or understood. New measurements are needed for commonly used low-Z, high-Z, open-shell and closed-shell materials, to be used as a gauge to test theory. More efforts at systematic assessment of theory are needed to provide a credible sub-keV database for the many activities at the national laboratories and for basic research.

Session 6B,1

Review, Session 2: Basic Theory Capabilities and Prospects

Richard Pratt

I don't plan to use the full time that you have offered me, but I might be wrong, so you had better keep track.

We are here trying to review Basic Theory, Capabilities and Prospects, and discuss where this may lead us. The instructions to the panel were not so much not to repeat what was already said, but to integrate it and say something about the future. I wrote those words before I knew I was going to have to do this.

In discussing basic theory we need specify the system we're talking about, which may be an atom or a molecule or a solid. We need some description of the dynamics that we are going to use to talk about that system. Typically, that system will have states of some sort. Then our interest is in various processes involving those states. This separation is not as clean cut, of course, as the words would suggest.

If we talk about systems, we can think of our atom in various ways. We know that, for some purposes, it is sufficient to talk of it as a continuous charge distribution. In both some classical calculations, and in certain versions or certain aspects of the more sophisticated theory, we describe our system in those terms.

At another level, and for many years, we have described our system in terms of non-interacting electrons moving in some fixed given potential. That was the model until a decade or so ago, I suppose, for the type of work we are discussing here.

And finally as we are hearing more now, our system must include, in many cases, the response to some external field, to some stimulus--in this case, to the presence of the photon in the process that we are talking about.

All three of these descriptions of systems then become more sophisticated when we must begin to talk about exchange properties of the constituents, or

correlations among the constituents, and we can discuss the aspects of exchange and correlation with respect to all three viewpoints.

The dynamics that we are discussing can be classical, quantum, or relativistic, or various versions of those three. We have not talked much here about classical dynamics, because historically most work on this subject began from the quantum viewpoint. It is possible, we now know, to go back and at least in a qualitative way understand many of the features of total absorption from at least a semi-classical viewpoint. Sometimes that classical viewpoint must have relativity added in it. Sometimes the quantum viewpoint must have relativity in it. Sometimes it is better if you leave it out. In addition, in all three of these versions of the dynamics, one at some point will have to become more sophisticated, including retardation, considering higher multipoles, etc.

Regarding states of our system, we heard quite a bit of discussion, beginning with Lloyd Armstrong's talk: the characterization of initial states and final states; the issues of channels; autoionizing states; other aspects of the continuum, such as the shape resonance phenomena. Further, in terms of trying to correctly identify the states, we need to talk about the issue of relaxation.

The processes we are talking about depend on the description of the system we have chosen and the states of the system as we have characterized it. Each such description usually implies various summations over things not observed, situations taken as indistinguishable within that description of the system. And the other side of that coin is that usually there are accompanying excitations, ionizations, further radiation, etc., which you have in any process you want to talk. It requires some decision both in terms of theoretical description and in terms of experiment to what extent you are summing over such things, to what extent you are ignoring them, to what extent they are within your experimental resolution or not. The characterization of the processes is also not unambiguous since we must discuss relaxation, Auger processes as separate processes or not, post collision interactions, etc. All of that, as we have been hearing, is involved in describing the process.

As for the theoretical approaches that we have been talking about on the classical side, some of Inokuti's work was mentioned. Also, the original Kramer's formulas are examples. There is literature on classical Thomas Fermi approaches and the like. The non-interacting electron approach, which as we said was fairly standard in this field a decade or so ago, was not much discussed here except, as we heard, it still is the basis of much of the tabulation work. Most of the current interest, at least in this soft x-ray regime, is in how to go beyond that central potential approach. Lloyd Armstrong gave us an alphabet soup, or at least the first letters of it: CI's, multi-configuration Hartree Fock, many body perturbation theory (which we then heard further about from several people, particularly Hugh Kelly, who was applying it to the discussion of additional excitation, double photo-effect, processes). R-matrix methods were mentioned but not too much discussed here.

The alphabet soup does continue. The fashionable method of a year ago, the RPA, which Walter Johnson talked about, has had many successes in explaining details of some of these processes while in the last year or so, having one or two failures. We have now heard about the time dependent local density approximation (TDLDA) approach, beginning with a local density approximation. This differs from the RRPA approach in beginning with a different initial unperturbed description of the system, but then proceeding with the same general type of further treatment. In this approach some of the correlations have been put into the starting point, whereas in RPA the exchange, but not the correlations, are in the starting point. We heard about this particularly from Andrew Zangwill, also from Walter Johnson and from Nancy Del Grande presenting some of Göran Wendin's calculations.

A separate issue that goes beyond these calculations, is the question of relaxation. We heard about that in new work of Zangwill and for example, in the types of things James Scofield was talking about.

There are major problems left: the field is not finished. One thing that bothers me is that, as theorists, we are relying too much on experiment to tell us whether we have a decent approximation to the underlying basic theory. We ought to be able to make up our own minds whether we think we have got a good theory and then do the comparison with experiment. But we haven't

succeeded in doing that yet. There is little control from theory on the accuracy of our approximations that accuracy is mainly being gauged from experiment.

We don't too well understand the regions of validity of the various dynamics--the classical, the quantum, etc., and how those transitions are made and when one or the other is sufficient. It doesn't matter, of course, for a process that is simple enough, or if you have big enough computers. But, if you want to insert calculations of these kinds into bigger problems, or say you understand what your computer did for you, it would be nice if we had a little better understanding of those regions of validity of dynamics.

Similarly, we all somewhat understand the implied sum rules that are involved as we go from one description to the next more sophisticated description, which suddenly allows many more states, many more processes to be occurring. But, I don't know that this has ever been worked out in a really clear-cut fashion, so that we can, beyond handwaving, say when those sum rules are reasonable, and when do we really have to be doing something better.

Clearly, we don't yet have a good understanding of what the most suitable starting points for perturbative approaches are. We are learning that in many cases that the local density starting point may be more suitable than the Hartree Fock starting point. Was there any way that we should have known that in the first place? Is there any way to say what is optimal as a starting point, or is it somewhat accidental?

Relaxation, it seems to me, is an issue that requires further discussion. One needs a comprehensive viewpoint that tells you, let's say, that at high energy you presumably start with unrelaxed states, whereas at low energy in some sense everything has relaxed before you are through with it.

There are all sorts of failures at high energy, which we didn't talk about much here. We did note that there seems to be a conflict as we went to higher energy between these otherwise rather impressive LDA based results and simpler results which do appear to be good at high energy. There are other problems that you get into as you go to higher energy, beyond the energies talked about here. Associated with them is a problem that does already occur

at these energies: namely, as we know how to describe things better, there is too much to describe. We need more effort to understand how to characterize what would appear to be voluminous data, and detail what the essential parameters are in terms of which everything else in some simple way follows. Life gets worse at higher energy, where you have more polarization properties, more multipoles, and so on. But, even here, we've been hearing about these very voluminous printouts from the TDLDA type theory, which suggests the same sort of problem: that having lots of numbers is good, but it is not the end of it. In some sense it is the beginning, as I always try to persuade my graduate students.

Now in concluding, let me present the only viewgraphs (see Figure 1 and Figure 2) that I was actually given from the session that I am reviewing. I think these are a useful set of viewgraphs just to remind you of some of the real issues that I have talked about rather vaguely and schematically. These are for the work on Uranium that Nancy Del Grande was talking about. They illustrate regions where there is general agreement on all theories, at high energies, for instance, where the simple one electron theories and some of the better theories are coming into line, and experiment is also more or less in line. At lower energies one has a region where the newest theories sort of agree with each other, and as Nancy said are at least within 60% of the available data from Cukier and Dhez. In part of this region, as I tried to bring out in asking Nancy a question, Henke's tabulation does not represent real data but interpolation across a region where there is no data. In this region there is also some old data, which I understand is now generally agreed should be repeated. The message is that over most of the high energy region we have quite good agreement, but there are other regions where there may be sixty percent or so type questions to talk about. At low energies these new theories we've talked about are very important. One sees that the single electron theories bear no resemblance any more to what is happening. The various effects of the correlations have become dominant by this regime.

Figure 1

Uranium photoabsorption cross sections
(G. Wendin and N. Del Grande, 1984)

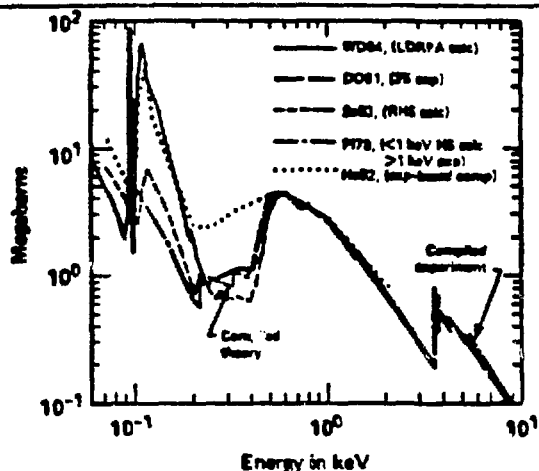


Figure 2

Uranium photoabsorption over giant 5d-d
dipole resonance region

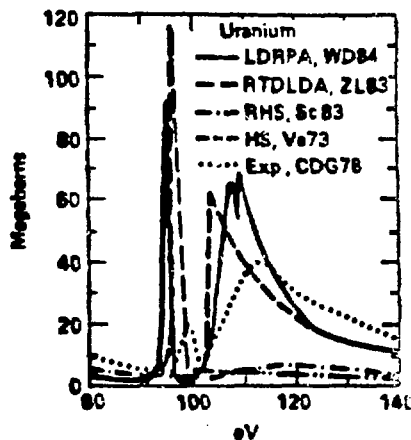


Figure Legends

Compilations of experimental data

He82, E > 30 eV
B. Henke et al., 1982

Hu71, E > 100 eV
J. Hubbell, 1971

McM69, E > 1000 eV
W. McMaster et al., 1969

P178, E > 1000 eV (exp)
E. Flechaty et al., 1978

Ve73, E > 1000 eV (exp)
W. Veigele, 1973

We81, E < 600 eV
J. Weaver et al., 1981

Calculations

ZL83, E > 80 eV, RTDLDA
A. Zangwill, D. Liberman, 1983

SC73, 83, E > 80 eV, RHS
J. Scofield, 1973, 1983

Ve73, E > 100 eV, HS
W. Veigele, 1973

WDB4, E > 60, LDRPA
G. Wendin, N. Del Grande, 1984

Measurements

CDW74, 130-450 eV, 50-100%
M. Cukier et al., 1974

CDG78, 76-130 eV, 30-50%
M. Cukier et al., 1978

DOB1, 844-3000 eV, 3%
N. Del Grande, A. Oliver, 1981

WG74, 80-140 eV
C. Wachenkel, B. Gauthé, 1974

We81, 90-120 eV
J. Weaver et al., 1981

In summary then, theory has certainly made great strides in the last decade, and the developments we've heard about here, I think, are very exciting. But I still claim there is a long list of problems to keep us busy for a few more months.

Thank you.

DISCUSSION FOLLOWING SESSION REVIEW

Q (QUESTION) R (RESPONSE)

QUESTIONS AND ANSWERS

Q: (James Scofield, Lawrence Livermore National Laboratory)

I didn't think Wendin's calculations were the same as the local density calculations.

R: (Nancy Kerr Del Grande, Lawrence Livermore National Laboratory)

Andy Zangwill spoke as though they were essentially the same. Wendin did not include the same relativistic effects. But, it turns out that in the region where the calculations were made, this was not very important.

Q: (Scofield)

I was asking about the basic theory; I thought there was a more RPA calculation.

R: (Pratt)

This is a local density calculation. Of course, Wendin had been doing RPA earlier, but as I understood it, this was a local density based calculation.

R: (Del Grande)

Göran Wendin describes his calculation as a local-density based RPA (hence, LDRPA). Andrew Zangwill and David Liberman describe their calculation as a relativistic time-dependent local density approximation or a

linear response approximation (hence, RTDLDA or LRA). Figure 2 shows that the results of these independent calculations were similar for Uranium at 80-140 eV.

Q: (Pratt)

What part of the Henke tabulation for uranium represented real data, and what part was interpolation?

R: (Del Grande)

Data at 80-130 eV (by Cukier et al., 1978) used by Dr. Henke to empirically adjust theory (by Veigele, 1973) verified the order-of-magnitude many body effect calculated by the local density approximation (LDA) theory (see Figure 2). Burt Henke used other data at 130-450 eV (by Cukier et al., 1974) which were ambiguous, may have had large systematic errors from unfiltered harmonics, and should be remeasured. These data were 3 times larger than LDRPA calculations (by Wendin) and 6 times larger than RHS calculations (by Scofield) shown in Figure 1.

Q: (Pratt)

Are there other data apart from what Henke used for the tabulation?

R: (Del Grande)

Not from 200-800 eV. At 840 eV to 10 keV there are 3% measurements (by Del Grande and Oliver, 1981). These data are typically 10-20% lower than the tables by Henke et al., 1982; within $\pm 5\%$ of RHS or IPA calculations (by Scofield or by Liberman); and 5-10% lower than RTDLDA or LRA calculations (by Liberman and Zangwill, based on their corrected results).

Q: (Troy Barbee, Stanford University)

I make things with atomic layers and so on. I am interested in what cross section effects one might see if you run out say a monolayer of uranium, in a quasi non-interacting matrix, and then look at that. Would you see two-dimensional effects in the cross sections?

R: (Pratt)

By my definition, this wouldn't be basic theory, but it would be the next step. Does anyone have any comment on whether you would expect any two-dimensional effects at those energies? I would be surprised.

Q: (Gary Doolen, Los Alamos National Laboratory)

The discrepancy at high energies (i.e., 1-10 keV) was mentioned, and I thought it might be nice to quantify that. See Figure 3a. So, I plotted Nancy's data which appear to agree more with the upper, independent particle model curve than with the lower, local density or linear response approximation curve. The question is, why. For, the two calculations differ by about 50% uniformly across the range. Nancy concedes that there may be what percent error?

R: (Del Grande)

Experimental errors were 3%. There was one region where there wasn't the typical 2-5% agreement with Jim Scofield's RHS calculations. This was near 4 keV, between the M_3 and M_4 edges, where theory was 15% higher than the data. Also, theory gave larger oscillator strengths for 3d-5f transitions than measurements.

Q: (Doolen)

So, it looks like there is a 30% discrepancy between linear response approximation or local density calculations and your experimental data still. That is the order of shake-up and shake-off. Maybe that is a possible explanation. [Editorial comment: David Liberman corrected the programs at LLNL and LANL which had been treating exponential functions improperly at the higher energies from 1-10 keV. The corrected U calculations in Figure 3b are within 5 or 10% of the experimental data, apart from near-edge regions, as shown in Figure 4. The linear response approximation, based on a time-dependent local density theory (RTDLDA or LRA)

agrees with the independent particle approximation (IPA) theory and with the 3% LLNL measurements for Ni, Sn, Ta and Au at 1-10 keV as shown in Figure 5. The LRA and IPA calculations differ for Mg, Cu, Ag and Au at sub-keV energies as shown in Figure 6.]

Figure 3

Differences between theories and 3% experiment before (3a) and after (3b) program errors were corrected.

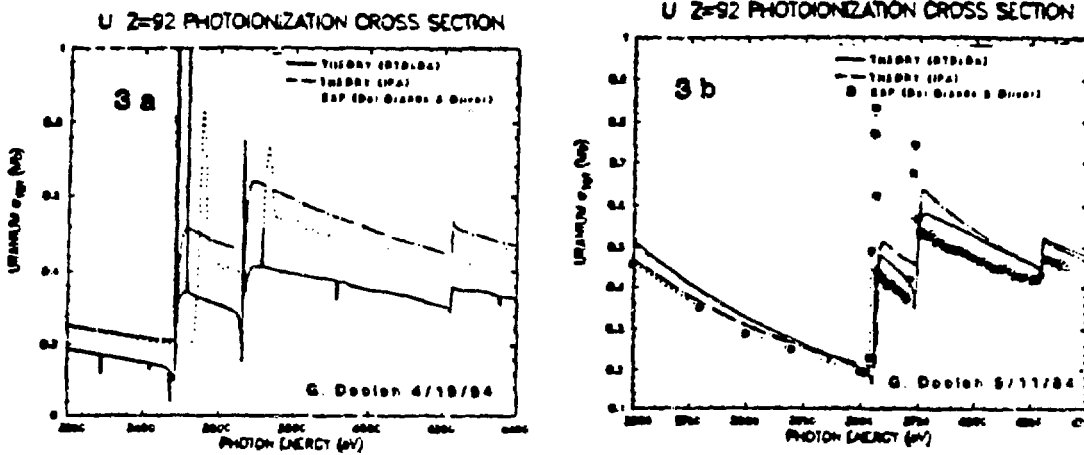


Figure 4

Comparison of theory with 3% experiment for U after correcting LANL/LLNL code

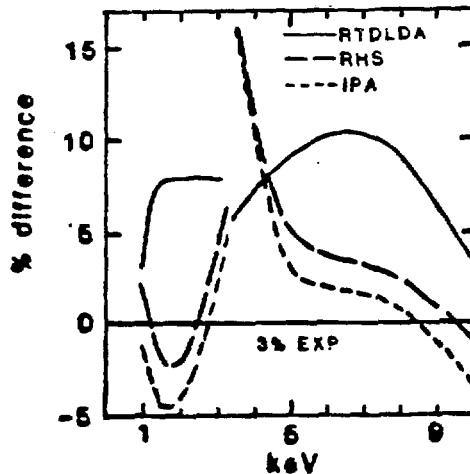


Figure 5

1-10 keV region showing agreement between local density and independent particle approximation theories, using experimental data as a gauge (after Doolen, LANL).

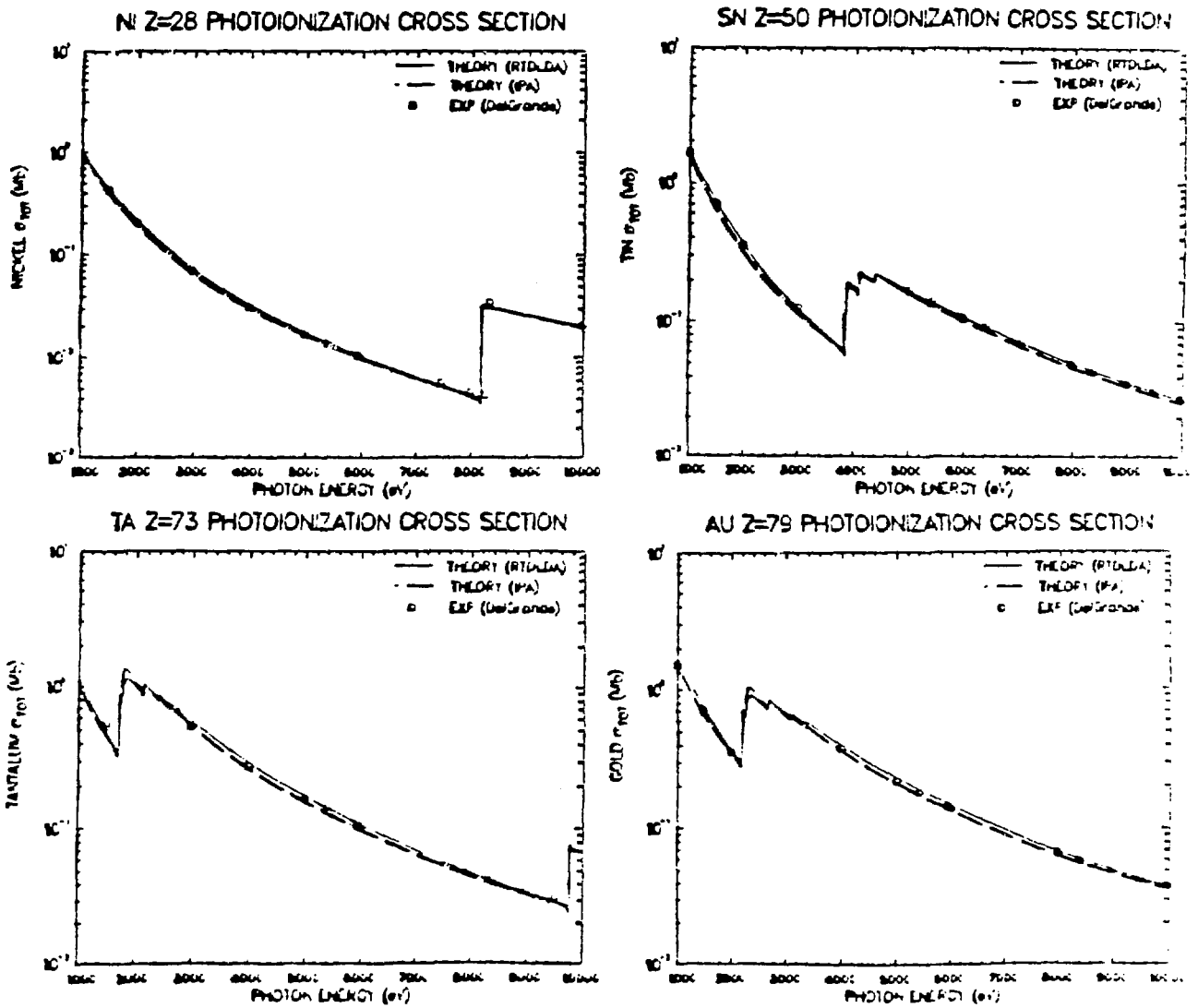
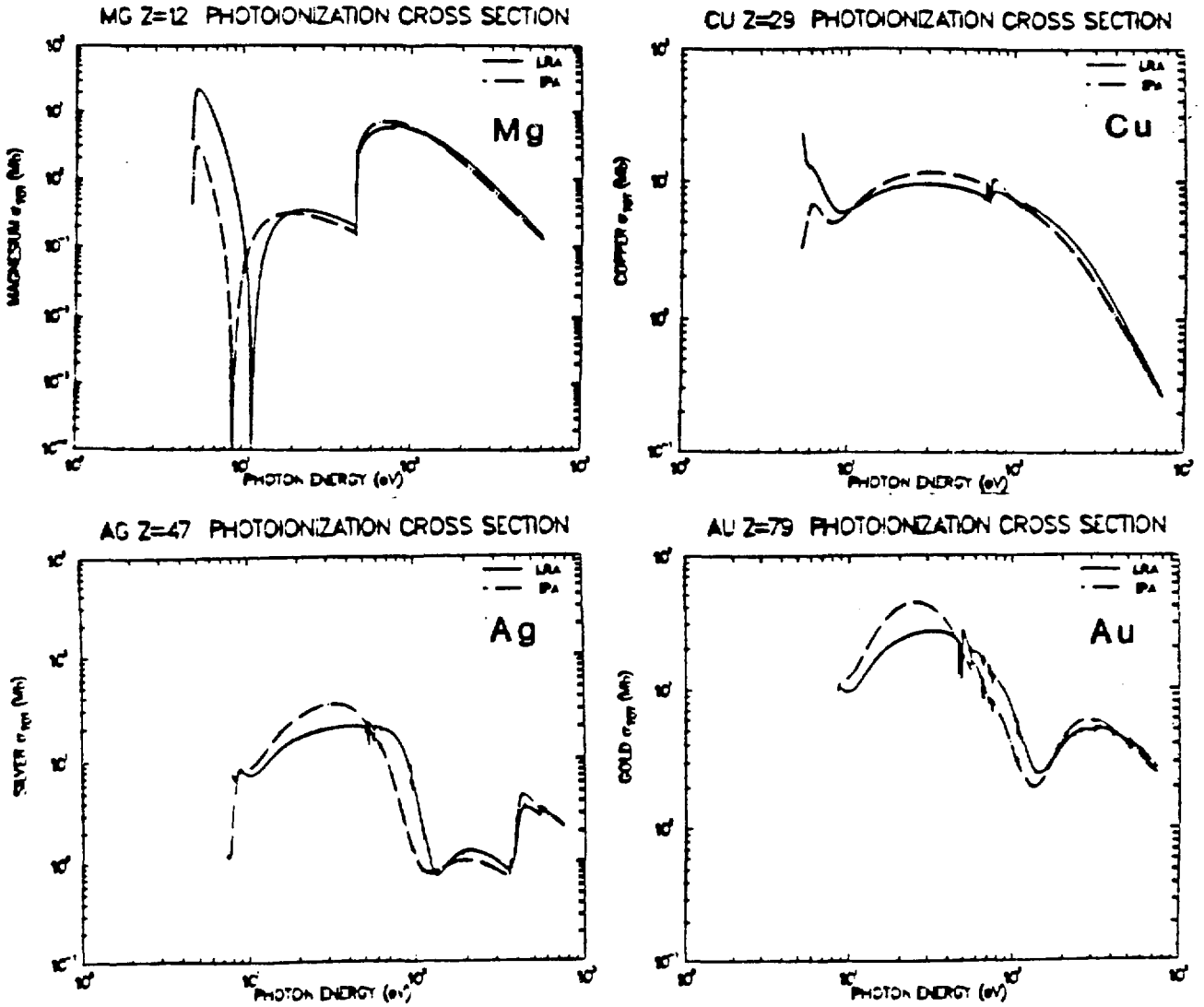


Figure 6

Sub-keV differences between LRA (linear response) and IPA (independent particle) theories (after Doolen, LANL).



Q: (A. L. Merts, Los Alamos National Laboratory)

It seems to me the electron scattering people have been arguing for a long time that the exchange correlation used in the density functionals is not right. It is for high energy. That is, if you do electron scattering off of atoms, and if you use something like the Wenden electron-electron correlation functions, one universally gets bad inelastic scattering cross sections. I wish Andy Zangwill was here to comment on that, but I wonder if anyone else would care to comment on this.

R: (John Rehr, University of Washington)

We have found that, for deep core hole processes it is essential that we use somewhat different exchange correlation potentials at high energy since the energy dependence reduces the effect of exchange dramatically from threshold. I just wondered what effect that had in other calculations? It would be very easy to incorporate this into the TDLDA, for example.

R: (Pratt)

It would seem unlikely that the effects are that big. We noticed many years ago, comparing some results with Jim Scofield's, that different versions of local exchange can lead to effects of a few percent, which will persist at all energies. This was a constant normalization effect, in L-shell photo-effect in aluminum. Effects of that kind would be smaller for inner shells or higher Z-elements. An effect I've heard about from some of the people at Sandia when we were doing Bremsstrahlung was that in our lightest elements, and at energies in the kilovolt region and below, there could be effects at the 4-5% level. I could well believe effects of the kind you are talking about, particularly, at the lower energies, and at the few percent level, but not something that is a constant, going up to several kilovolts, and in higher Z-elements.

Q: (Merts)

I believe the experience of people doing electron scattering is that the high energy effect can make an increase in inelastic scattering cross

sections by electron impact by as much as 40 or 50% at high energy due to the exchange. Correlation doesn't go to zero because of identity. But, of course, the interactions of the electron are long, long range. This was for inelastic electron scattering. I don't think it comes into the elastic electrons, and I don't know whether it would affect the continuum photo-electron wave function.

R: (Pratt)

But that becomes fairly unimportant in the photo-effect at high energy. Because, in the photo-effect you are dealing with the inner region as you go to high energy, not this outer region.

Session 6B,2

Review, Session 3A: Effects of Environment on Cross Sections
for Molecules and Solids

Ingolf Lindau

There is a dilemma in trying to put this session into proper perspective, because, if one would then like to make a comparison between what theory is predicting for atoms, one has a handful of problems in doing so, as we have heard in earlier sessions. If one would like to extend it to solids, there are a number of additional complications. Nevertheless, I think we have made a lot of progress in studying the effect of environment on the cross section.

For photoabsorption experiments, impressive progress was reported by Dr. Rehr in terms of the theoretical analysis of EXAFS data. As you know, the EXAFS technique is being used to do structure determinations and get information about the bonding distances between atoms in molecules and solids. Dr. Rehr discussed, in his talk, the effects of the inelastic scattering processes in these kinds of determinations. This represents a very important further development in applying this technique to structural determinations.

Dr. Albers discussed, in his talk, the EXAFS effect very close to the ionization threshold which is the part of the spectrum usually called the near-edge structure. Traditionally, one has excluded the first 40 to 50 eV or so of the spectrum close to the threshold from the EXAFS analysis, because it has been too difficult to interpret. The work by Dr. Albers is extremely important, because a wealth of information about both the electronic and the structural properties is available from the near-edge absorption data. In Dr. Albers' analysis, the near-edge data is bridged with the EXAFS modulations at higher energies. I am confident that we will see much more of this approach in the future, and I think that it will add tremendously to our understanding of the solid state effects in photoionization cross sections.

The remainder of the talks in this session mostly addressed the effect of the environment on outer valence levels. I would first like to make a general comment. Very little has been done in comparing one and the same partial photoionization cross section for the solid and metal vapor phases. For the

few cases where it has been done for the deeper lying core levels, there seems generally to be fairly good agreement between the results for solids and the theoretically predicted values from atomic calculations. One has, thus, been quite successful in using atomic calculations in analyzing the energy dependence of partial photoionization cross sections for solids.

In terms of studying effects of the chemical environment on the cross section, there were two particular areas which were discussed: resonance photoemission and the so-called Cooper minima effect. Resonance photoemission is really a very broad concept which can be applied to a number of different situations. In its broadest sense, it refers to the situation where the onset of the excitation of a deeper lying core level results in the enhancement of the emission from some other electronic levels in the system, e.g., more shallow core lines or valence levels. Dr. Zangwill discussed the former case for barium. When you turn on the excitation from the 4d core level, there is strong enhancement in the cross section from the 5s and 5p at the onset of the 4d ionization threshold (see Figure 7). Dr. Zangwill also described the many-electron theory which at least qualitatively takes care of that phenomenon (solid line in Figure 7). The way the resonance photoemission manifests itself in the experimental cross sections was discussed by Dr. Weaver. It is shown schematically in Figure 8 for a system with an open 4f shell structure. The cross section is plotted against the photon energy. The delayed onset of the 4f emission due to the centrifugal barrier is denoted as "cross section enhancement" in the figure. When the 4d threshold is reached at about 115 eV, a very strong enhancement is observed in the cross section, the resonance photoemission effect. For ytterbium oxide, which has a f^{13} configuration in the ground state and one empty 4f level, the resonance can be described very satisfactorily with a classical Fano resonance, i.e., one discrete state interacting with a continuum (see Figure 9). For a more complex multiplet structure of the 4f configuration, the resonance will contain additional fine structure, but the basic features of a Fano resonance remains.

Even if the detailed physical mechanisms behind the resonance behavior are not well understood, it can be used as a spectroscopic tool with many applications, e.g., determination of the binding energy position of 4f levels,

the occurrence of mixed valence states on surfaces, and the changes in sp-d hybridization upon compound formation. The determination of the 4f binding energy position in Ce was discussed by Weaver and is illustrated in Figure 10. The photoemission valence band of Ce is shown for a number of photon energies between 80 and 130 eV. Around 120 eV, which is the binding energy for the 4d levels, one particular peak in the valence band goes through a strong emission enhancement. This is the resonance photoemission effect, and the peak can be assigned to the 4f level. The area under this peak would mimic a Fano resonance quite well (see Figure 9). Spectroscopically, one is thus able to identify the orbital character using the energy dependence of the cross section.

Figure 7. Resonance photoemission for Ba.

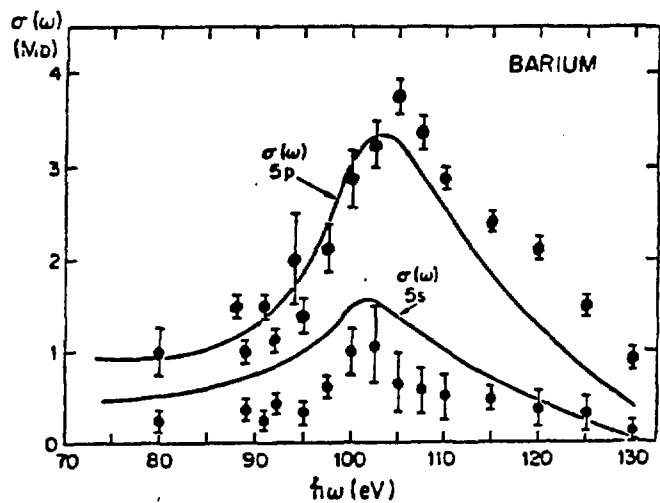


Figure 8. Resonance photoemission for Ce.

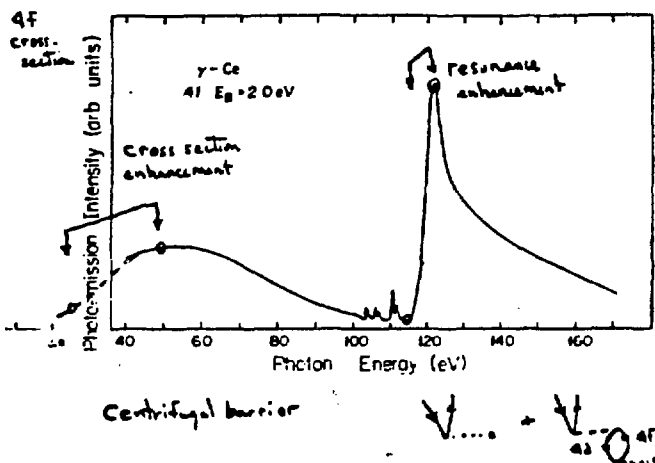


Figure 9. Example of a classical Fano resonance.

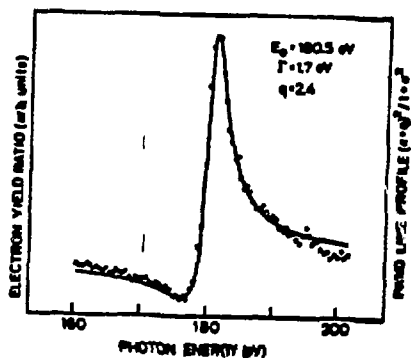
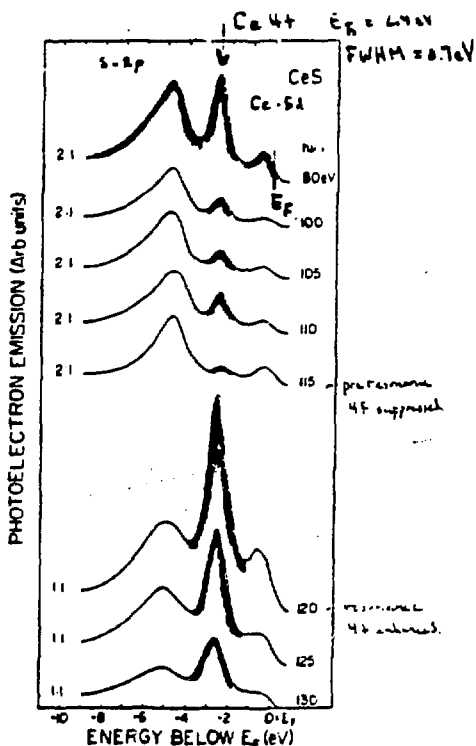


Figure 10. Photoemission valence band of Ce.



Zangwill illustrated with some experimental data by Allen, et al., how the resonance photoemission effect can be used to study mixed valence states on a samarium, Sm surface. Mixed valence states are a quite common phenomena for rare-earth metals and compounds and arise from the fact that one 4f electron fluctuates back and forth, resulting in two different configurations. These configurations are very sensitive to the environment. The 4f valence structures associated with Sm 2+ or Sm 3+ will both show a resonance behavior when the photon energy is tuned through the 4d photoionization threshold. But, the fine structure in the resonating cross section is distinctly different for the two configurations $4f^5$ and $4f^6$. Thus, the mixed valence states can be distinguished unambiguously with the resonant photoemission technique. This is illustrated in Figure 11 which shows the experimental data by Allen, et al., and a calculation by Zangwill.

The second topic which was discussed in terms of the effects of the environment on the cross section was the so-called Cooper minimum. The Cooper minima shown in Figure 12 and Figure 13 occur for wavefunctions with nodes and show up as a rapid variation of the cross section, typically within the first 150 eV above the threshold. Quite naturally, the cross section is very sensitive to changes in the environment. Dr. Carlson discussed this for molecules in the session on "Insights from Related Phenomena." As Dr. Carlson showed in his talk, it is more convenient for atoms and molecules to study the effect of the environment on the energy dependence of the asymmetry parameter β . At this point, it is not clear what happens to the asymmetry parameter when the atoms are in a solid. In fact, we do not even have information about how chemisorption of molecules on surfaces will affect the asymmetry parameter. Therefore, we are presently limited to examine what the effect of the solid state environment is on the partial photoionization cross section. But, it is possible to distinguish the bonding d-orbitals from the anti-bonding orbitals. This will serve as the final example, where the solid state environment has a very pronounced effect on the cross section (See Figure 14).

In summary, we have shown that the solid state environment can have very strong effects on the energy dependence of the cross section and can affect its absolute values very significantly in certain energy regions. So far,

very little has been done theoretically to understand the solid state effects. From a spectroscopic point of view, we have seen cross section measurements develop as a sensitive analytical technique to probe very subtle changes in the solid state environment.

Thank you.

Figure 11. Distinguishing mixed valence states with resonance photoemission.

4f partial cross sections (theory vs. experiment)

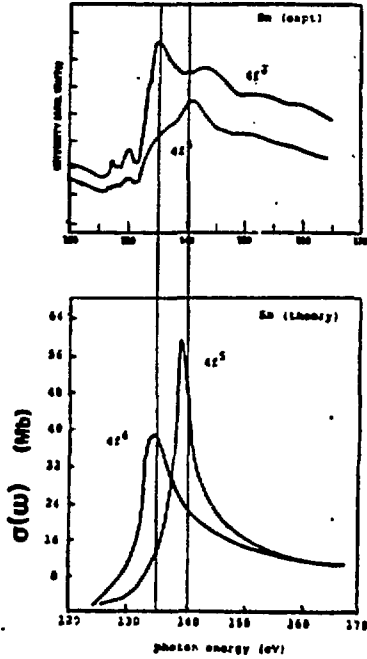


Figure 12. Cooper minima.

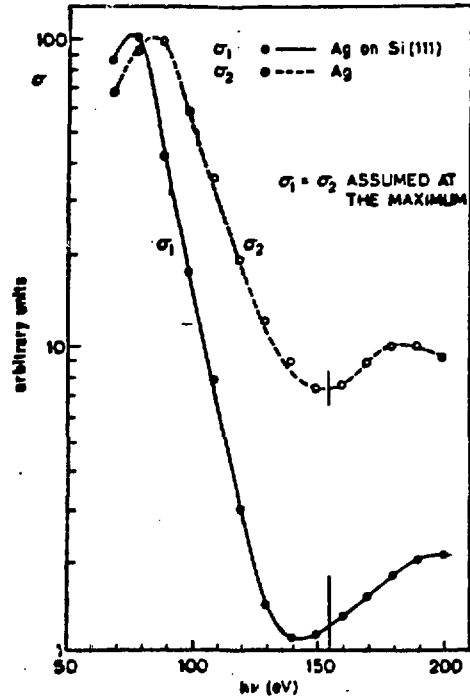


Figure 13. Examples of Cooper minima.

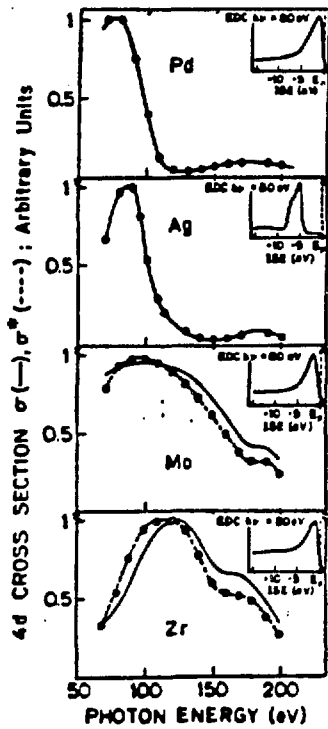
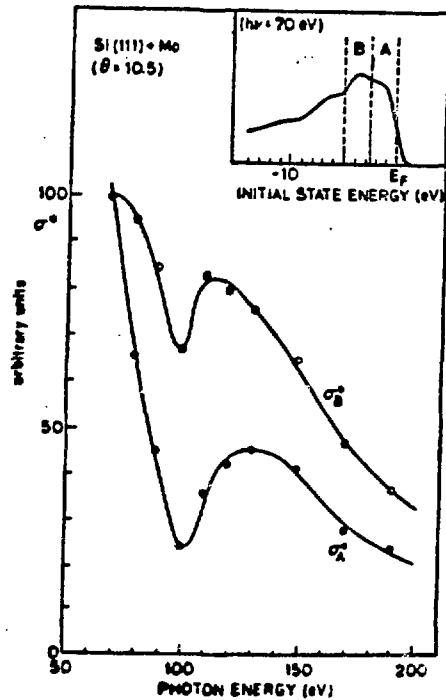


Figure 14. Effects of the solid state environment on cross sections.



Session 6B,3

Review of Session 3B: Effects of Environment on Cross Sections
for Excited States and Ions

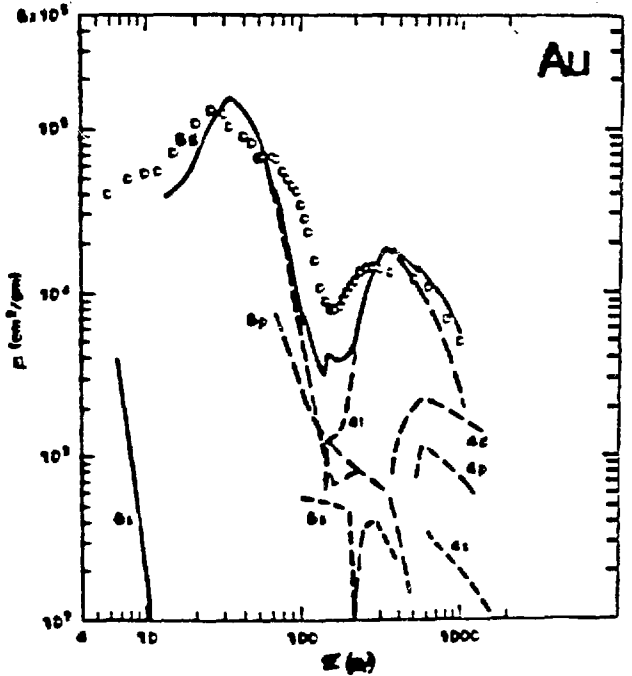
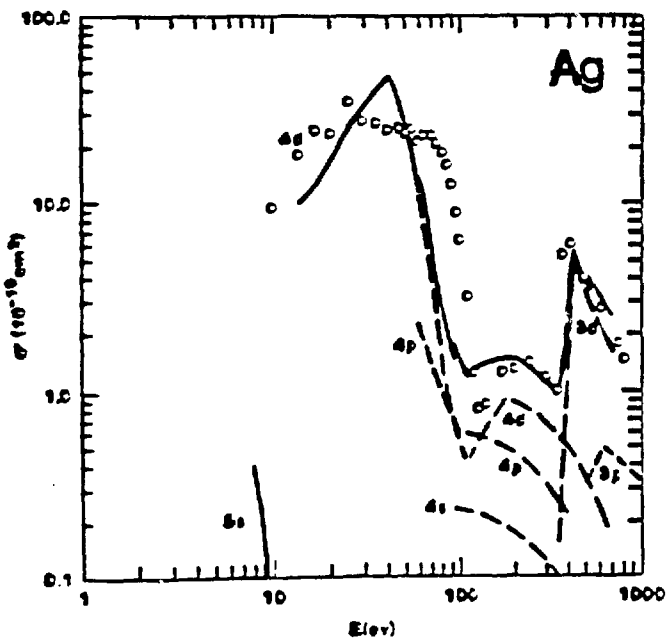
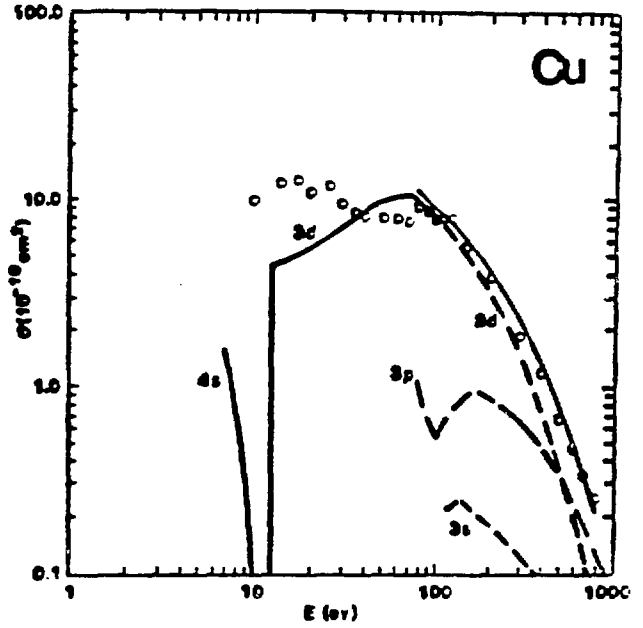
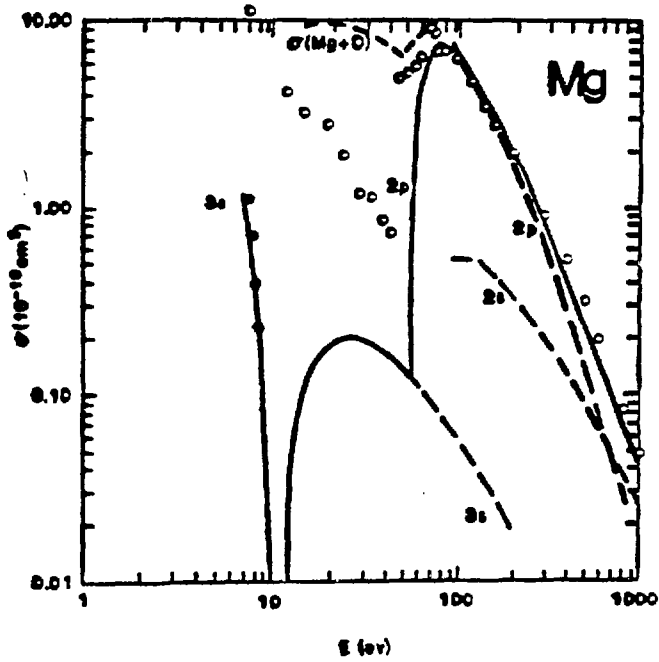
A. L. Merts

In this session the problem is considerably different than where one is talking about the measurement of photoabsorption of isolated atoms or isolated molecules. One generally has an environment, basically a plasma, in which the interactions may come from a material that is at least as dense as it is in a normal solid. The environment is even more hostile, because the temperature can range from room temperature up to a kilovolt. So that one has to deal not only with the multi-electron atom, but one has to talk in some sense about the interaction that takes place between the other atoms and ions of the plasma as well as the free electrons. Nevertheless, the starting point is coming up with the basic cross sections for the fundamental entities, namely the atoms and ions. Gary Doolen has made a fantastic start on that, using a model in which he calculated something like 400 different ions and atoms and transported the information here. You have heard the comments on what various people think about the model. Like the Herman Skillman model, this model gives results which one can compare with other models pretty well across the whole range of the atomic table. Examples for Mg, Cu, Ag, Au from Doolen's comparisons of linear response and independent particle models and from McGuire's comparisons of the Herman Skillman model with DESY synchrotron data are shown respectively in Figure 6 and in Figure 15.

Partly at my suggestion, Doolen looked at some excited states of iron at about 30 eV, and I don't want to make any comments on that, except that when we picked the magnesium ion as the most abundant ion, he found that only 14% of the population was in the $3S^2$ state. So that when one is dealing with photoabsorption or any other interaction process in the plasma, the atoms or ions may be in excited states. What Gary has done is to compare the linear response approximation calculations for photoabsorption with independent particle model calculations. One certainly sees differences and these were talked about in Dick Pratt's session here. Gary also put some of them on the

Figure 15

Sub-keV differences between HS theory and DESY synchrotron data (after McGuire, SNL).



board for us this morning. In addition, you see electron resonance structure that occurs in the model. Clearly, one doesn't have adequate experience either in comparing the results with experiment or with the results of detailed models. You can see how realistic these comparisons are in a number of cases, since our gauge seems to be comparison with experiment. I think that this is a step forward in the sense that it is a mechanism that allows us to get a large number of cross sections for elements across the periodic table.

In Dick More's discussion, he tried to parameterize the properties of the plasmas. Since Dick left without giving me any of his viewgraphs, he will have to suffer the consequence if I paraphrase a number of things that he said. One of the important parameters that he talked about was the plasma coupling parameter, $\Gamma \equiv Z^2 e^2 / R_0 kT$ in Figure 16, which is basically the interaction energy of the ions at a given temperature, T , and mean separation, R_0 . One can characterize strongly coupled plasmas by whether this parameter is large or small. For many of the applications, such as laser-heated plasmas, to name one, this parameter can range from larger than unity to .01, with .01, characterized as a weakly coupled plasma. Another parameter useful for dense plasmas, $\gamma = E_F/kT$, is essentially the ratio of the Fermi energy to the temperature of the system. When the parameter is large we say that it is degenerate. When it is small we say that it is non-degenerate. Of course, you have all of those intermediate states in between. Some have interesting consequences which we don't have time to go into today.

There was still a third parameter, which I guess has not really been given a name, but it has to do with the overlap with the wave functions of those states that are claimed to be bound to the ions. If one does a very simple calculation and looks at the value of the wave function and the derivative of the wave function at the mid-point between ions, one can make a reasonable estimate of when the energy levels associated with the system are beginning to deviate from atomic-like values. If one puts them in a lattice, one can get an estimate of the density at which the level will start to spread due to the interaction of the neighboring ions. Generally, what one finds in most thermal plasmas is that the ionization in the plasma is such that only

Figure 16

ION-COUPLING PARAMETER Γ

$$\Gamma \equiv \frac{Z^2 e^2 / kT}{R_0}$$

← distance of closest approach
← actual neighbor distance

Ideal plasma has $\Gamma \ll 1$ Dense plasma has $\Gamma \geq 1$

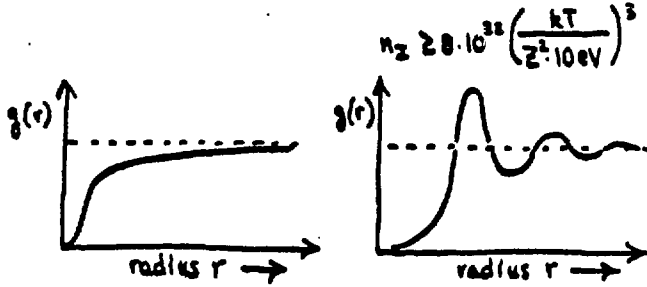
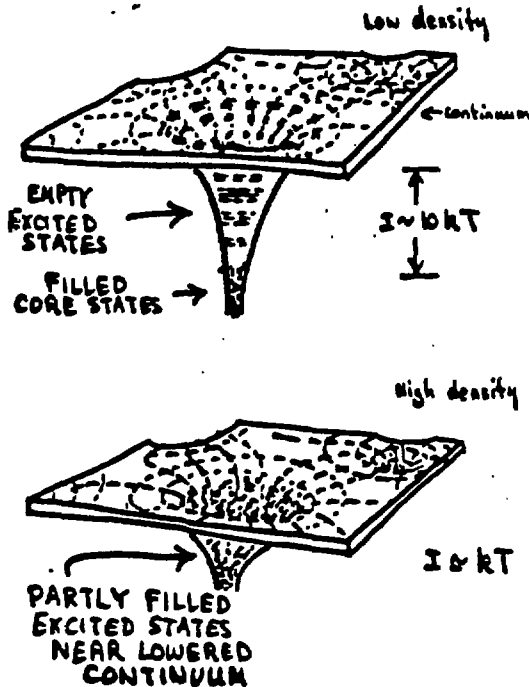


Figure 17

Schematic of the local potential well and bound state levels (after More, LLNL).



the highly excited states of the atom show appreciable broadening due to this effect. There are obviously always collisions with various ions and the fluctuating micro-fields which we won't go into at present.

Dick showed in Figure 17 a two-dimensional effect trying to characterize what happens to the levels as you go into more dense systems. What is shown schematically in Figure 17 is the local potential well, and the bound state levels that exist. As the density gets higher and higher, the screening from both the neighboring ions and electrons affects the potential relative to the free atom which is lowered. This is called continuum lowering in the language of plasma physics. What it really means is that a number of those levels of the isolated atom do not now exist as bound states. A problem with most models is that of permitting a discontinuous ionization of the ion as a function of plasma density. However, one does not see a discontinuous change of the character of the wave function from a bound state into essentially a continuum-like state. What one usually sees is resonances in the continuum which still maintain a fair amount of their bound state character. This resonance structure is sensitive to the model. Therefore, one wants to be a bit careful about believing atomic models for shape resonances, because one can get some fairly profound shape changes from small model changes.

Dick Fortner's talk had to do with plasmas in a slightly different sense. Not only does he observe the radiative processes but he observes the electron-ion processes. As he mentioned to you in the talk, what he is really interested in is the rate coefficients. If one looks at the time evolution of the plasma, what are the contributing processes that are important? One has the radiative recombination where the electron colliding with an ion becomes captured. Since we consider an infinite mass nucleus we consider energy conservation but don't have momentum conservation in recombination. This is an important process for moderately dense plasmas. For higher densities, eventually one will run into a situation in which the electron collides with an electron in the neighborhood of an atom, or an ion, and recombined without giving off a photon; this is called three body recombination. The important thing to remember is that there are two electrons involved, and the importance increases with density like the square of the electron density. This is the inverse process of collisional ionization.

Then another process, though, which is fairly close to a number of processes that have been talked about in this conference, is dielectronic recombination. Dielectronic recombination, as you know, is usually referred to as an independent two-step process in which an electron, incident upon an ion, excites say a core electron, and is captured into a meta-stable state that may auto-ionize. Actually, as Dick mentioned, if that is all that happened, you just simply have a complicated scattering process because it auto-ionizes and continues in the continuum. But, a second step in the process usually treated as independent, is for one of the electrons to drop down to the lower state so that the ion is now stabilized. This is what is usually referred to as dielectronic recombination. That is after the radiative relaxation has taken place.

An important feature is the branching ratio. If you prepared it in this doubly excited state that it can auto-ionize or it can radiatively stabilize. The branching ratio should be the possibility that the ion will auto-ionize rather than radiatively stabilize. For neutral systems, for which most of the measurements have been made, the auto-ionization is very rapid compared with the radiative de-excitation. So that basically, the sum is just the counting of states; the branching ratio is very nearly one in most cases. This has some important consequences; the auto-ionizing rate contributions are largely from lower angular momentum partial waves. However, in the presence of a constant electric field, angular momentum is no longer a good quantum number and one mixes at fairly low fields all ρ 's for a given principal quantum number, n . The branching ratio can change rather dramatically in the presence of the field.

The second point is that the experimentalist sees a given line. On the low energy side, usually, there are circumstances where this can invert, but almost always the line has asymmetry. This is caused by a large number of states in the high Rydberg series for the second electron which are so close in energy that one can't resolve them. Then, as you go to a lower energy, one begins to see those auto-ionizing states which are separated enough from the resonant line that one can see them. It is important to remember two things. First, one has to identify which of the lines in the plasma are really auto-ionizing lines emitted by the plasma. Secondly, the conditions on the plasma can have a fairly big effect.

In a thermal plasma it is not easy to determine from the observed radiation alone whether one is observing dielectronic recombination or the excitation of a core electron of an already excited ion. The impact of the incoming electron exciting a core electron can prepare the same auto-ionizing state. If you simply look at the emerging photon there is no way that one can distinguish between whether that photon came as a result of dielectronic recombination or as a result of excitation of an already excited ion. So that this method would not be trustworthy to determine the cross sections, or the rate coefficients. The point that I want to emphasize, and the point that Dick was making, is that in a certain range of temperatures and densities this double excitation or dielectronic recombination can be the most important recombination process in the system.

One frequently finds under plasma condition that the dielectronic recombination exceeds the radiative recombination by factors of 50. The first example of where this was, of course, is the solar corona. Here, one had a huge discrepancy between the temperature inferred from comparisons of the continuum radiation and the intensity of certain lines in Fe¹⁵.

Now in contrast to the conditions in a plasma, Tu-Nan Chang in his talk advocated that one can simplify the interpretation using a two-step process. One uses two sources, a laser and some other source like synchrotron radiation. One can excite the outer electrons to a specific state and then look at what happens to the absorption from a second source. One can produce resonances that, if you pick your radiation at the right frequency, can prepare states corresponding to a specific configuration and then study the photo processes. Tu-Nan Chang also pointed out in his talk that if one is talking about the photo processes, photoionization say, from a system in which the outer electron has been excited, then the simple minded picture of the frozen core processes seems to work acceptably well. However, when we get to processes in which we have holes in the core, then perhaps one is in a situation where the best techniques that we have may not be adequate.

Our last speaker, David Nagel, made the point that laser heated plasma sources, if one is interested in photons of energy less than about one kilovolt, deserve considerable attention. If indeed, one can get away with pulsed

sources, that is where you zap a target with a laser and generate a hot source, then his contention is that these are really in competition with the synchrotron radiation sources. Secondly, he proposed as an application measuring in-situ absorption and emission of the hot plasma. One of his suggestions was that one simply zap a material and look at the emission out at the end as a function of length. As he pointed out, the emission is eventually going to saturate, because once the radiation is emitted from one mean free path, then the intensity becomes independent of length.

Another suggestion, which in principle is certainly acceptable, is that one considers a source of one material looking at the transmission through a second material. He pointed out that one can look at absorption as well as amplification "in principle" through this process. In practice, I think, one has some of the same difficulties that I have mentioned before concerning a plasma system for measurements. First of all, it is very hard to define exactly the temperature and the density of the plasma. Since the cross sections certainly depend on the temperature and the density through the level abundance, it is not clear how useful such measurements really are. This process has some promise as a useful source, especially for those people who are doing plasma diagnostics. I think, however, that one ought to be aware that for cross sections there is considerable uncertainty in the crucial plasma parameters.

DISCUSSION FOLLOWING SESSION REVIEW

Q (QUESTION) R (RESPONSE)

R (Richard Pratt, University of Pittsburgh)

I might just comment that we have verified with a single electron calculation that if you excite a core level and then ionize, that indeed you can no longer rely on the common curves that Tu-Nan Chang was showing.

Session 6B,4

Review, Session 4: Experimental Capabilities and Prospects

Roger Bartlett

Let me give you the one-line summary first. That is, absolute soft x-ray photoabsorption measurements are difficult but, if state-of-the-art apparatus and techniques are brought to bear on the problem, measured absorption values with accuracies in the range of 1 to 5% can be obtained.

Figure 18 is a schematic representation of a generic system to measure photoabsorption. It includes a photon source, monochromator and filter systems to produce a pure monochromatic photon beam, a well characterized sample, an energy discriminating detector, and a data acquisition and control system. The measurement procedure usually involves measuring the transmitted beam intensity through the sample and the beam intensity without the sample, both as a function of photon energy. The two signals are divided giving the transmission from which the absorption is derived. Such a system and the problems associated with it were discussed by Glenn Tirsell. Other talks in the session covered synchrotron and transition radiation sources, unique sample configurations (transmission gratings and multilayers), crystal monochromators and two-dimensional detectors. Also, some aspects of the experimental situation were touched on by John Weaver and Pierre Dhez in an earlier session.

I will discuss each of the items listed in Figure 18 starting with the source.

Synchrotron sources were discussed in the early part of the session by Walter Trela. Their salient features are listed in Figure 19, each of which is highly desirable for making absolute measurements. I will say a few words about each feature.

Stability. Stability in both time and position are highly desirable. Variations in intensity as a function time can usually be corrected for by an intensity monitor in the sample chamber. Variations in beam position may merely cause variations in intensity; however, they may also cause shifts in

the photon energy that exits the monochromator. The effect will depend on the monochromator being used. The more stable the beam, the less stringent the requirements will be on the intensity monitor and the smaller the photon energy variation.

Synchrotron sources (storage rings) are quite stable compared to conventional sources; however, many storage rings are not as stable as one would like and a beam monitoring system is necessary.

Continuous Spectrum. Synchrotron sources produce a continuous spectrum from the IR to the x-ray region. With a monochromator this produces a tuneable source--a necessity for observing structure in the absorption spectrum. The continuous spectrum does, however, contribute to harmonic and stray light.

Intensity. For most absorption measurements, the intensity from a bending magnet synchrotron (storage ring) source is more than adequate; however, for some gas phase and cross beam experiments, more intensity is desirable and wiggler and undulator sources are preferred.

Collimation. Synchrotron sources are highly collimated compared to other sources in the soft x-ray range. Vertical divergences of approximately 1 mrad are typical but vary with photon energy and with electron energy in the storage ring. The collimation plays an important role in monochromatizing the beam as discussed by Paul Cowan.

UHV Compatible. The UHV compatible vacuum offered by synchrotron sources is important in two ways. One, it reduces carbon contamination of the optical elements in the system and two, it reduces sample contamination. Preparing samples in an ultra-high vacuum environment and maintaining that environment throughout the measurement is very important for absolute measurements. A small surface contamination on a thin film can be a significant part of the sample.

The other source that was talked about was transition radiation. It is schematically represented in Figure 20. In this case, one starts with a relativistic electron beam and passes it through a periodic structure. In the

Figure 18

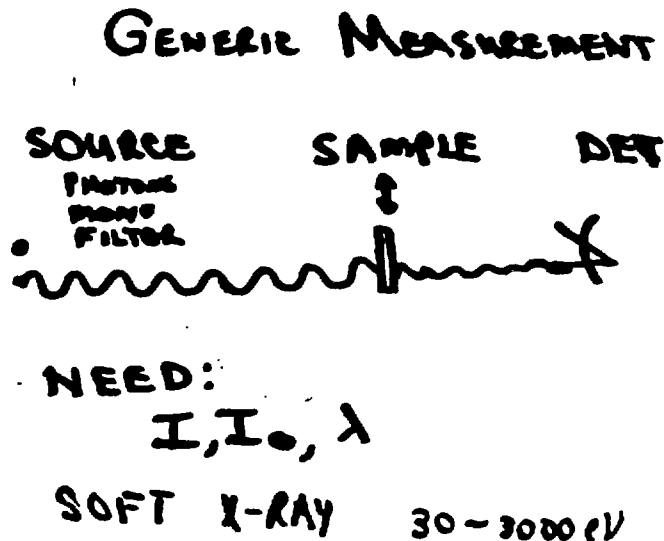


Figure 20

Figure 19

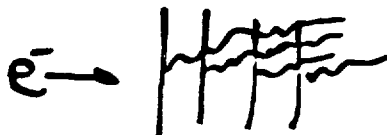
SR SOURCES

- STABLE (TIME & SPACE)
- CONTINUOUS
- HIGH INTENSITY
- COLLIMATED
- UHV COMPATIBLE
- AVAILABLE NOW

[ALL SOURCE]
[WIGGLER]
[UNDULATOR]

TRANSITION RADIATION

- CONTINUOUS
- STABLE ?
- HIGH INTENSITY
- COLLIMATED
- UNDER DEVELOPMENT
- LOWER COST
(THAN SR)



cases discussed beryllium foils were used. Multilayers, as described by Troy Barbee, may also work. The radiation produced is continuous. It has short term stability or at least I believe it could be made so. However, I am not sure about the long term stability which may deteriorate due to damage caused by heat and the electron beam. The source intensity is on the order of bending magnets from synchrotrons for the same electron currents. It does have some collimation. I assume that this is a function of the number of layers in the foil stack that one is using. This source is under development at the present time. I think that the advantage in the future will be a lower cost, and therefore, I assume more of them will be around. This is important because the problem with a lot of the measurements in the past is not that the sources haven't been adequate, but that there hasn't been adequate time to use the sources. As mentioned by Walt Trela, when one goes to a synchrotron one is under the gun, and a preprogrammed approach is all that can be carried out. Many measurements in the future are going to be improved merely by the fact that we will have more sources available and more time on these sources.

Both of the sources discussed are essentially continuous in energy. In order to do most measurements, one needs a monochromatic beam. Two papers in the session discussed aspects of monochromatizing a continuous source. Glenn Tirsell talked about several grating instruments and Paul Cowan discussed a crystal monochromator for the soft x-ray range. It is clear that for the soft x-ray regime there are added difficulties imposed on the monochromator design. Just the vacuum requirement alone adds complexity to the instruments. The soft x-ray transition region where grating type monochromators are reaching their high energy limit and crystal monochromators are up against their low energy limit. Recently the energy gap between the two types of instruments has narrowed and, in fact, now their energy coverage overlaps. This has been accomplished by improvements in gratings, both better ruled gratings, and the relatively new ion etched holographic gratings and by the use of large d spacing crystals such as beryl.

The crystal monochromator discussed by Paul Cowan is an excellent example of the advances that are taking place in monochromator design. The instrument has a fixed output beam, particularly important when large UHV sample chambers

are used. It is UHV compatible, has high resolution and will work down to approximately 800 eV.

The next element in the generic system is the sample. There were no talks in the session about thin film samples even though they are the most common form. John Weaver mentioned a few of the problems commonly associated with thin films, a few of which are surface contamination, uniformity, pinholes, and determining the density.

Talks that did touch on the sample problem were given by Roman Tatchyn and Troy Barbee. Their talks covered two new sample configurations. Tatchyn discussed transmission grating samples. His analysis showed that optical constant data derived from measurements of the zero and first order grating transmission were less sensitive to random defects and surface contamination of the sample. Also, both the real and the imaginary part of the index of refraction were derived from the data.

In Barbee's talk, we heard about multi-layers and their uses as samples. Because a series of layers are participating in the measurements (reflection or transmission), and that these layers are isolated from the outside environment, the measurements are not affected by surface contamination nearly as much as in the case of a single thin film. Because Barbee can make a number of types of structures, I think this opens the way to many new measurements. For example, he has been able to make Fabry-Perot etalons, which may be used to measure optical constants in the soft x-ray range.

The final element that I will discuss is the detector. Here one looks for linearity, dynamic range, and uniformity over the active area. I think, particularly in reflectance measurements, the cathode uniformity is often overlooked. The sensitivity of the cathode is usually not very uniform across its surface, thus, causing errors in normalization if different parts of the cathode are used. One would also like an energy selective detector system so that harmonics and stray light that were not eliminated previously would be discriminated against at the detector itself. In some measurements, the technique of choice is photon counting using an electron multiplier or a channeltron, and a multi-cathode system so that one can pick the cathode response to discriminate against unwanted photons.

We did hear a talk in the session about a two-dimensional detector by Tom Callcott. It was made from conventional parts, which is always a nice feature. It had very low noise characteristics, good dynamic range and could be made UHV compatible.

In summary, the capability exists to measure absolute photoabsorption cross sections in the soft x-ray energy range to an accuracy of 1 to 5%. To do this, however, will require the use of state-of-the-art components throughout the measuring system and will require careful sample preparation and handling.

Synchrotron radiation sources coupled with the latest innovation in monochromators and filter systems are the "best" photon sources in the soft x-ray regime at the present time. The major difficulty has been the lack of time available on these sources for absolute photoabsorption measurements. Also, the lack of funding for cross section measurements has been a major difficulty.

DISCUSSION FOLLOWING SESSION REVIEW

Q (QUESTION) R (RESPONSE)

Q: (Paul Cowan, NBS)

Several times in this conference people have cited stability in synchrotron sources. I suppose stability is a relative term. But one point that I failed to make in my talk yesterday is that in order to get this sort of high-resolution performance that was being predicted there, that it is really necessary to characterize the stability of your source in terms of its position, its beam size, the beam current, and so on, continuously, both the monochromator and in the experiment itself. Although the synchrotron itself may be stable for most things, if you are going to push the technique you better not rely on the stability provided by the machine physicists. You need to build in your own stability in the way that you take the data.

R: (Roger Bartlett, LANL)

Yes, I agree with that.

Q: (Nancy Del Grande, LLNL)

I think what was interesting, as I have heard from several people, is that the general community hasn't really recognized the need to put an effort into better than 30%, or so, cross sections in this region. John Weaver mentioned that his emphasis had been changed from photoabsorption measurements. I heard from Pierre Dhez that, in France, the situation was similar. Do we have any comments on this, or any thoughts of who might change this situation, if there was a need?

R: (Bartlett)

I will make a comment. From my point of view, maybe we don't need absolute measurements across the whole 92 elements, but one would like to have at least good measurements on say a low-Z, high-Z, open-shell, closed-shell system, or whatever is necessary for a good check of theory, so that one can actually pin down the theories. And then let the theorist crank out all of the numbers. There is no sense competing with Gary Doolen. I don't want to produce, 10^4 curves at a synchrotron. So, one would like to pin down and find out where the errors are. But once that is done, then I would like to calculate the rest. Also, many of the measurements are sample-dependent, so that if you are actually building some kind of an optical element, one would like the optical constants to an accuracy that will allow an estimate of the response of the optical element. But once that is done, I think you are going to have to measure the element anyway. Because, its surface characteristics, roughness, contamination, etc., are going to affect its responses.

R: (Roman Tatchyn, SSRL)

I just have a qualitative observation. Speaking for myself, I also feel that it is very viable to pin down optical constants in the soft x-ray range to as high a precision as can be had. Not just for the sake of metrology, which is one of the foundations that comes with physics, but

because we have a practical need for x-ray optics in this range. Before one can design or evaluate systems accurately one needs the constants. I, myself, intend to pursue this little method that I was talking about for as many materials as is possible. Indeed, efforts are being made right now, for example, between Berkeley and IBM to launch a program that will investigate the manufacture of transmission gratings of different materials. Now any such work, of course, will require funding. A large precondition for it going anywhere is that when the proposals are written that they receive favorable reviews, so money will be granted. So, I just encourage open heartedness on the part of the community, so a lot of these techniques will proceed if we in any way have a screening influence for that process.

Thank you.

R: (Pierre Dhez, Université de Paris-Sud)

I think we missed something to recall here. And I wish to refer to the talk presented by Chris Brion. I feel that the comparison with his technique, with the energy-loss spectroscopy, will be very helpful to debug all the artifacts we have in our measurements.

I am sure that it will enable us to understand many, many details. For example, the different uranium numbers between the theory and the experimental measurements. If Chris can do something, I think that we would have many, many questions. So, I think we must remain open to this kind of thing.

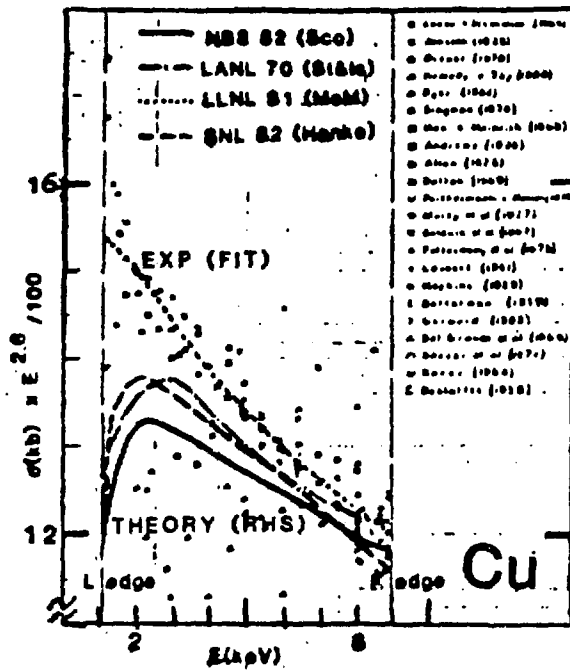
R: (Bartlett)

This paper was not in Session 4 and will be reviewed elsewhere.

[Editorial comment: Some of the artifacts we have in our measurements were noted by John Hubbell (see Figure 21) and by Eugene McGuire (see Figure 15) in the session: Efforts at Systematic Assessment and Tabulations, which occurred just prior to the review of previous sessions.]

Figure 21

1-10 keV region showing differences between tables based on theory or measurements for Cu (after Hubbell, NBS).



Session 6B,5

Review, Session 5: Insights from Related Observations

Steve Manson

In Session 5 we talked about various other ways of obtaining information on photoabsorption; ways that involved the photoabsorption process, but not measuring the x-ray or photon attenuation directly. And in some sense, these are actually superior ways of learning about it, from the point of view of comparison with theory. I will get to the various ways in a second, but when, as I said last night (some of you may actually have been awake to hear it) when you make a photoabsorption measurement and then compare it with a theoretical calculation, you can come to one of two conclusions. It agrees or it doesn't agree. If it agrees, well everything is "hunky-dory." We theorists tend to, you know, keep calculating until we agree with the experiment, and until such time as experiment changes, we don't do any more in that area.

But if it doesn't agree, to begin with, then we are faced with the problem why--doesn't it agree? Is it that the whole theory is no good and we are doing all the pieces wrong? Just remember that in a theoretical calculation, by-in-large, you calculate all the pieces and you add them up. What these related insights, that Session 5 talked about, this is how to get information on some of the pieces; some of the individual channels, let me call them. This is because, the photoabsorption is the sum of these individual channels. And there are various techniques and I would just like to go through them rather briefly to emphasize their importance.

Perhaps the most important one is under the general name photoelectrons spectroscopy. Dennis Lindle talked about that, Tom Carlson talked about it, and in his own inimitable way Chris Brion talked about it, except there we have to put the "photoelectron" in quotes. I will come to the e-2e method in a moment. Anyhow, you see the photoelectron spectroscopy technique allows you to look at each one of the individual channels to the extent of your resolution. And then, you see, when you make comparisons with theory you can say, well, these five channels agree--this one doesn't or something like that.

Now there are many types of processes you can measure. When you are doing a photoabsorption measurement, the only variable you really have, for a given sample, is the photon energy. But when you are doing photoelectron spectroscopy, for each photon energy, you see a whole bunch of lines; sometimes you see a continuum which you call background and may not in fact be background in the sense of noise, but background in the sense of, like for example, a double ionization process, where you have two or more electrons sharing the energy, and so neither one of them has a fixed energy, and that sums up as a continuum or a background. But this is not noise. Tom Carlson and Manfred Krause many years ago showed us many of the details of this sort of thing.

It was pointed out that these measurements can tell you a great deal about details. Particularly, when you do it with something other than the 584 line. Not that there is anything wrong with the 584 line, but it is very difficult to assess a theory based on one energy point. Even I can get it right if there is only one energy point. A crucial aspect is the variation with photon energy.

Now there are other ways of doing business. A rather neat way which Jim Samson talked about was, if you are doing something other than the outer shell you create a vacancy and if you don't look at the photoelectron, you can look at the filling of the vacancy by a photon; this is fluorescence work. Fluorescence work was popular some years ago, particularly in the visible. The reason it hadn't been used very much for photoionization in the soft x-ray range or the VUV range, is because spectroscopy in that range is tough. There are not very good filters, or whatever. It is a difficult business, but certainly possible. And not only that, you can get some details that are very difficult to get out of photoelectron spectroscopy. For example, the thing that Jim brought up, consider helium ionization plus excitation (not that helium is so very important, but it is a good laboratory because things are relatively simple and you can pick out the channels relatively easily) where you look at the channel where one electron has been ionized and another has been excited to the $n = 2$ state. Well, the 2s and 2p states are degenerate from our point of view, Lamb shift and this sort of thing. We don't have the

tools just yet to be able to resolve that in photoelectron spectroscopy; the Lamb shift is pretty small. But what one can do, using fluorescence spectroscopy, what you are looking at is the radiation downward. Now the 2s does not radiate downward. (Actually, sits there for a good long time, but it does radiate downward, but not enough to worry about.) It is a metastable state whereas the 2p goes lickety-split down to the 1s and you can see that. So, by using a combination of the techniques, photoelectron spectroscopy to get the total in the $n = 2$ states and then the fluorescence spectroscopy, you can pick out individual pieces. As a matter of fact, most of the comparisons of this process with theirs, and there has been a fair bit of controversy about this particular process, deal with the sum of everything left in $n = 2$, the ratio of that to the main process where things are left in the 1s state. Now, we have pretty good ways of breaking it down into 2s and 2p to see, for example, is the theory doing good in one and not in the other. I don't want to get into the details which is right and which isn't, but it is this sort of fine detail that makes these tools very very valuable to be able to assess the utility of the theory. As a theorist, I can tell you that without corroborative evidence, never believe a theorist. You know, in law unsubstantiated testimony is viewed with great distrust and rightfully so. The law has had lots of experience with that. Most newspapers won't let a reporter write an article saying something, unless he got the information from one source and corroboration from another source. We need corroboration.

Pierre Dhez mentioned the sort of (e, 2e) work that Chris Brion does, with what I would call a poor man's synchrotron. He would call it a poor man's synchrotron. (It is not that poor. Let's say a bourgeois synchrotron. I mean it is still not that cheap, right? If you are below the poverty level; forget it, you can't have that either.) This technique makes use of the fact that if you have a fast electron and a relatively small energy loss of that electron in the collision process it looks very very much like a photon, with the energy loss being essentially the photon energy. There are some slight differences, but not very many actually.

In principle, if you did spin analysis you can even do spin polarization; mock-up spin polarization spectroscopy of the photoelectron. It is a little

bit trickier because then you have to make sure that the incident electron didn't change its spin, but aside from that it is a technique that only requires a small energy loss which implies relatively small momentum transfer. You also detect in the forward direction. Again, I don't want to get into the technical details about how this is done. Chris talked about that. But this offers a way, simply another way, of looking at exactly the same processes. You can do both photoabsorption as well as photoelectron spectroscopy. Again, with the "photoelectron" and the "photo" in sort of quotes, but all of the comparisons that have been made so far, where we believe say the synchrotron work, the comparisons are excellent.

This technique as Pierre pointed out, would be very useful if in particular cases where there may be a problem with the synchrotron data for one reason or another. For very small energies it doesn't offer the resolution that the synchrotron does and yet on the other hand its resolution is fixed. It is not a $\Delta\lambda/\lambda$ kind of resolution, but it is a fixed energy resolution, and even when you are looking at say a kilovolt energy loss--equivalent to a kilovolt photon--at that point I think the resolution is somewhat better than, what one generally uses on a synchrotron. Now on a synchrotron, of course, if you are willing to sacrifice counts, you can have essentially infinitesimal, magnificent resolution. However, you may get a count a month, so you pay for it.

There are other ways to go. Auger spectroscopy and the Auger process were talked about. When you have a vacancy in the inner shell, you can look at fluorescence down to it. However, it is often true that the fluorescence yield which is roughly the percentage of the decays of that hole that go by a radiative process, in a near-outer shell is pretty small. So there aren't too many photons. However, if the fluorescence yield is small the Auger yield is large. Most of the vacancies decay via an Auger process. Then, it becomes much easier to do Auger spectroscopy. However, it gives you the same sort of information that fluorescence spectroscopy might give you. Now, if you are dealing with a type of process like Paul Cowan talked about, when its a K-shell in argon, there you begin to get a reasonable fluorescence yield--about .2 or so. However, if you are doing the L-shell of argon, it is .01 or

maybe .001. It is possible, but difficult to use fluorescence spectroscopy there because you don't get many counts; you get a lot more intensity if you do Auger spectroscopy. But in order to do the Auger spectroscopy, you need to know something about branching ratios and rates and that is what Mau Chen talked to us about last night--well, he actually talked about fluorescence yields--as a matter of fact. If you know the fluorescence yield, you have a chance of making cross sections absolute, by doing the Auger spectroscopy, but you have got to know the fluorescence yield. Actually, the same thing applies to fluorescence spectroscopy, be it the VUV or x-ray region. If you don't know the fluorescence yield, you have no hope of making it the cross sections absolute. Even if you know them, you may not be able to do it for other reasons, but at least you need to know that.

Okay, now from a completely different point of view we also heard about x-ray scattering at relatively high energy x-rays. Nevertheless the interaction is the same. Some of the same information that you get from photoabsorption you can get from x-ray scattering as Dr. Templeton talked about. Aside from other things, he pointed out that crystallographers have a great need for some of this data, which translated means there may be some funding for rather basic atomic work, for applied use. That is always nice. One thing in his talk that particularly interested me, and I would like to emphasize it, that using two different polarizations on an oriented sample gave rather vastly different results. I must confess, I don't know enough about molecules, but to me it was somewhat surprising. I expected there to be some difference, but not as different as it was.

Okay, to sum up the summary then, let me just say that there are these various ways of getting other information about the process of interaction of photons with matter and it is really the sum of all of these processes which gives us the photoabsorption. And these are collateral, because when you sum over all the processes that you can have at a given photon energy, if you haven't made any mistakes, what you must get is the total photoabsorption--photon attenuation, which are synonymous at low energies. I realize that they are not at high energies, MeV energies, but in the soft energy range, for our purposes, they are synonymous. These techniques are, how shall put it, moving

apace in that they are generating good data and useful data to answer some of our questions about whether the theory is any good, and if so, in what channels is it any good. But that is not the question that we really want to answer. The question is the reverse, in which channels is the theory bad and what can we do to fix it up? And so that, I think, was the main message of this session that I would like to leave you with.

Thank you.

DISCUSSION FOLLOWING SESSION REVIEW

Q (QUESTION) R (RESPONSE)

QUESTIONS AND COMMENTS

R: (A. L. Merts, LANL)

Yes, I would like to make a comment here that has some bearing on what you said. In your introductory remarks you mentioned that theorists frequently progress until they get "agreement with the experiment" and then quit. Dick Pratt also mentioned that we were relying heavily on the experiments. I think the danger with free parameters floating around is the fact that in pre-Kepler days if they had CRAYS, we would probably explain orbital motion of the planets as an expansion with a linear superposition of epicycles. Undoubtedly it would have agreed quite well with our basis set. So, I guess that all that I am saying is I think we need a lot of data. But, I would encourage the people who are looking at the theory to look beyond that. That is just one step on the road to a complete theory. You want to look and see what you have left out of the physics. I hate to say this, but I think that I have seen almost as many errors perpetrated from the experimental data as from theorists; because, there are at least as many ways to make mistakes there, as there are in theory.

R: (Nancy Del Grande, LLNL)

I think that the first step is getting theorists together with the experimentalists, maybe on a commonly interesting problem, independent of who made an error or which measurement wasn't quite so good. I learned a great deal talking to Andy Zangwill. I first took the approach that maybe in the 5d uranium resonance that there is some stray UV coming in, on the low side, broadening things, that would change the resonance shape. Andy said, the next step that they hadn't put in was the multiplet splitting which would have spread that line and broadened it. Hence, with reference to Uranium in Figure 2, he expected that the calculation would be narrower than the measurement. Just getting together and hearing how the theorists think, and the next step that they haven't put in yet, is a part of a learning process that broadens your perspective for the whole problem. I think communication is a really important step to solving some of the problems.

R: (Chris Brion, University of British Columbia)

I would like to stress what I think is becoming increasingly important; that is, the exploitation of sum rules to get absolute data. While it is probably very easy for us to do that with the virtual photon field as I explained last night, I think of the big improvements that have now come with wide range monochromators for UV light. This is an approach that the photon people should look at a little bit more, because it is a lot easier to do than a true absolute measurement. It also provides a consistency check upon that.

R: (Steve Manson, Georgia State University)

Yes, I absolutely agree with you. As a matter of fact, in a recent (about three years ago now) book by Joe Berkowitz, he takes a number of atoms and molecules, takes all of the extant data the he knew of, and he tries to reconcile the sum rules. You know there is more than just the single sum rule which you call, the sum of all the oscillator strengths which has to equal a certain thing, but there are various moments of the energy which

one can put in a sum rule to learn something about the consistency of the data in various ranges. To anybody who is interested in that, I would recommend Joe Berkowitz's book as just a way to learn the techniques--the kinds of things that one can do to data, but it must be broad data. If you measure data only at one energy, it will not help you.

R: (Gene McGuire, Sandia National Laboratory, Albuquerque)

I would like to make a comment with regard to the various light sources (synchrotrons) which have recently or will soon come on-line. These machines emit a very large amount of light. It seems to me that with so much flux, people should be thinking about doing various kinds of coincidence measurements; the count rate will still be high.

Appendix 1

Technical Program

Session 1: Opening Session

Sunday evening, 7:30 P.M.

Organization Host: John (Hal) Mallett, LLNL

John (Hal) Mallett - Welcoming Remarks

Nancy Del Grande - Announcements

Chair: Richard Pratt, University of Pittsburgh

- 1,1 Lloyd Armstrong - Overview of theoretical capabilities and prospects.
- 1,2 John Weaver - Review of low energy experimental situation (below 200 eV) and experimental techniques.
- 1,3 Pierre Dhez - Evolution of the status of absolute total photoabsorption measurements by means of synchrotron radiation (with range 0.1 to a few keV) and opening of new promising possibilities.

Session 2: Basic Theory: Capabilities and Prospects

Monday morning, 8:30 A.M.

Chair: Walter Johnson, Notre Dame University

- 2,1 Walter Johnson - Relativistic and many body effects in photoionization.
- 2,2 Andrew Zangwill - Overview of density functional approach.
- 2,3 Hugh Kelly - Inner shell ionization: interplay between Auger processes and double photoionization.
- 2,4 Kwok-Tsang Cheng - Shape resonances in inner shell photoionization.
- 2,5 Nancy Del Grande - Sub-keV uranium calculations versus experiment.
- 2,6 Vojislav Radojevic - Multiconfiguration Tamm Dankoff Approximation.

- 2,7 Balazs Rozsnyai - Inner shell photoionization in heavy elements.
- 2,8 James Scofield - Exchange effects in photoabsorption cross sections.

Session 3A: Effects of Environment on Cross Sections for Molecules and Solids
Monday evening, 7:30 P.M.

Chair: John Weaver, University of Minnesota

- 3A,1 John Weaver - p-d and d-f resonances and the effects of the environment.
- 3A,2 Ingolf Lindau - Solid state effects on practical photoionization cross sections.
- 3A,3 Andrew Zangwill - Resonant photoemission as a probe of local electronic structure.
- 3A,4 Robert Albers - Review of electronic band structure calculations of x-ray absorption and comparison to EXAFS calculations.
- 3A,5 John Rehr - Inelastic effects in EXAFS.

Session 3B: Effects of Environment on Cross Sections for Excited States and Ions.

Monday evening, 9:30 P.M.

Chair: A. L. Merts, LANL

- 3B,1 Tu-Nan Chang - Photoionization from excited atoms.
- 3B,2 Gary Doolen - Results and applications of linear response calculations.
- 3B,3 Richard Fortner - Time resolved plasma spectroscopy.
- 3B,4 Richard More - Dense plasma parameters and conditions.
- 3B,5 David Nagel - Laser-plasma X-UV sources.

Session 4: Experiment: Capabilities and Prospects

Tuesday morning, 8:30 A.M.

Chair: Paul Ebert, LLNL

- 4,1 Walter Trela - Characteristics of synchrotron radiation sources for investigating soft x-ray photoabsorption.
- 4,2 K. Glenn Tirsell - Experimental capabilities and problems at 240 eV to 1300 eV.
- 4,3 Michael Moran - Properties of transition radiation x-rays.
- 4,4 Paul L. Cowan - Crystal monochromators for synchrotron radiation from 800 to 5000 eV.
- 4,5 Tom Calcott - Use of two-dimensional detectors in x-ray spectrometers.
- 4,6 Roman Tatchyn - Optical constants of metals in the soft x-ray range from transmission-diffraction measurements.
- 4,7 Troy Barbee - Synthetic microstructures as samples for optical constant determinations.

Session 5: Insights from Related Phenomena

Tuesday evening, 7:30 P.M.

Chair: Dennis Lindle, LBL

- 5,1 James Samson - Fluorescence Spectroscopy.
- 5,2 Dennis Lindle - Photoelectron Spectroscopy.
- 5,3 David Templeton - X-ray Scattering.
- 5,4 Chris Brion - Photoabsorption and photoionization by electron impact.
- 5,5 Mau Chen - Auger and fluorescence yields.
- 5,6 Paul L. Cowan - X-ray fluorescence and scattering at the Argon K Edge.
- 5,7 Tom Carlson - What's next: Experiment.
- 5,8 Steve Manson - What's next: Theory.

Session 6A: Efforts at Systematic Assessment and Tabulations

Wednesday morning, 8:30 A.M.

Chair: Nancy Del Grande, LLNL

- 6A,1 John Hubbell - Review of current tabulations and the new I.U.Cr. x-ray attenuation coefficient project.
- 6A,2 Eugene McGuire - The need for calculations better than Herman-Skillman across the periodic table.
- 6A,3 C. D. Wagner - Apparent disagreements with theory on photoelectric cross sections by XPS experiments.

Session 6B: Panel Review of Sessions

Wednesday morning, 9:15 A.M.

Chair: Hal Mallett, LLNL

- 6B,1 Richard Pratt - Session 2:
Basic theory capabilities and prospects,
reviewed.
- 6B,2 Ingolf Lindau - Session 3A:
Effects of environment on cross sections for
molecules and solids, reviewed.
- 6B,3 A. L. Merts - Effects of environment on cross sections for
excited states and ions, reviewed.
- 6B,4 Roger Bartlett - Session 4:
Experimental capabilities and prospects,
reviewed.
- 6B,5 Steve Manson - Session 5:
Insights from related observations,
reviewed.
- 6B,6 Hal Mallett - Concluding remarks.

Appendix 2

List of Participants

Institution

Dr. Robert Albers	Los Alamos National Laboratory, Los Alamos, NM.
Dr. Lloyd Armstrong, Jr.	John Hopkins University, Baltimore, MD.
Dr. Troy Barbee	Stanford University, Stanford, CA.
Dr. R. J. Bartlett	Los Alamos National Laboratory, Los Alamos, NM.
Dr. Chris Brion	Univ. of British Columbia, Vancouver, B.C., Canada
Dr. Tom Callcott	University of Tennessee, Knoxville, TN.
Dr. Tom Carlson	Oak Ridge National Laboratory, Oak Ridge, TN.
Dr. Mau Chen	Lawrence Livermore National Laboratory
Dr. Tu-Nan Chang	USC, Los Angeles, CA.
Dr. Kwok Tseng Cheng	Argonne National Laboratory, Argonne, IL.
Dr. Paul L. Cowan	National Bureau of Standards, Washington, D.C.
Dr. Nancy Kerr Del Grande	Lawrence Livermore National Laboratory
Dr. Pierre Dhez	L.U.R.E., University of Paris-Sud
Dr. Gary Doolen	Los Alamos National Laboratory, Los Alamos, NM.
Dr. Paul Ebert	Lawrence Livermore National Laboratory
Dr. Richard Fortner	Lawrence Livermore National Laboratory
Dr. John Hubbell	Nat. Bureau of Standards, Washington, D.C.
Dr. Walter Johnson	University of Notre Dame, Notre Dame, IN.
Dr. Hugh P. Kelly	University of Virginia, Charlottesville, VA.
Dr. Yim Lee	Lawrence Livermore National Laboratory
Dr. Ingolf Lindau	SSRL, Stanford University, Stanford, CA.
Dr. Dennis W. Lindle	Lawrence Berkeley Laboratory, Berkeley, CA.
Ms. Loriann Lynde	Lawrence Livermore National Laboratory
Dr. John H. (Hal) Mallett	Lawrence Livermore National Laboratory
Dr. Steven T. Manson	Georgia State University, Atlanta, GA.
Ms. Janice L. Meamber	Lawrence Livermore National Laboratory
Dr. Eugene McGuire	Sandia National Laboratory, Albuquerque, NM.
Dr. A. L. Merts	Los Alamos National Laboratory, Los Alamos, NM.
Dr. Michael Moran	Lawrence Livermore National Laboratory

Dr. Richard More	Lawrence Livermore National Laboratory
Dr. David Nagel	Naval Research Laboratory, Washington, D.C.
Dr. Richard H. Pratt	University of Pittsburgh, Pittsburgh, PA.
Dr. Vojislav Radojevic	Univ. of Notre Dame, Notre Dame, IN.
Dr. John Rehr	University of Washington, Seattle, WA.
Dr. Balazs Rozsnyai	Lawrence Livermore National Laboratory
Dr. James Samson	University of Nebraska, Lincoln, NE.
Dr. David Shirley	Lawrence Berkeley Laboratory, Berkeley, CA.
Dr. James Scofield	Lawrence Livermore National Laboratory
Dr. Roman Tatchyn	Stanford University, Stanford, CA.
Dr. David Templeton	Lawrence Berkeley Laboratory, Berkeley, CA.
Dr. Lieselotte Templeton	Lawrence Berkeley Laboratory, Berkeley, CA.
Dr. Walter Trela	Los Alamos National Laboratory, Los Alamos, NM.
Dr. K. Glenn Tirsell	Lawrence Livermore National Laboratory
Dr. C. D. Wagner	Consultant in Surface Analysis, Oakland, CA.
Dr. John Weaver	University of Minnesota, Minneapolis, MN.
Dr. Andrew Zangwill	Polytechnic Inst. of New York, Brooklyn, NY.