ACTA UNIVERSITATIS UPSALIENSIS
Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science
292

DEVELOPMENT OF INSTRUMENTATION AND DATA ACQUISITION SYSTEMS FOR CHARGED PARTICLE SPECTROSCOPY. HIGH RESOLUTION STUDIES OF ATOMS AND SMALL MOLECULES.

by

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UPPSALA 1990

Doctoral dissertations at Uppsala University 1990
ISBN 91-554-2648-4
ISSN 0282-7468

Abstract

Carlsson Göthe M., 1990. Developments of Instrumentation and Data Acquisition Systems for Charged Particle Spectroscopy. High Resolution Studies of Atoms and Small Molecules. Acta Univ. Ups., *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science 292*. 30 pages. Uppsala. ISBN 91-554-2648-4.

The redesign of a UV photoelectron spectrometer for gas phase photoelectron, Auger electron and ion fragment spectroscopy is described. Outer valence studies have been carried out for several small molecules. The spectrometer has also been adapted and used for Doppler free coincidence studies on ion fragments of diatomic molecules.

Inner valence studies of atoms and molecules using HeII radiation have, up to now, been limited by the intense HeI induced background. A new monochromator for HeII has been built which enables a large extension of the useful energy range in UV photoelectron spectroscopy. The focusing properties of the toroidal grating gives no reduction of the intensity of the HeII radiation after monochromatization. High resolution studies have revealed several new molecular states in N_2, O_2 and CO. A high resolution photoelectron spectrum of Xe is presented which exhibits approximately 70 states previously not observed in photoelectron spectra. Valence studies of formaldehyde, acetylene and methane are also presented.

Two data acquisition systems have been developed. The usefulness of Ada in scientific applications and modern software engineering principles are discussed.

A portable distributed run time system for scientific real-time applications written in Ada, has been designed and implemented. The system allows an application to be pre- and/or post partitioned and to run on a loosely coupled system. The program units that may be distributed are tasks, task objects, packages, procedures, functions and variables. Task objects may be dynamically distributed. The system has a high fault tolerance due to unit redistribution.

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To BRITT-LOUISE and HANNA.
To my parents.

1. LIST OF PAPERS

I	**Optimization and Redesign of an Electron Spectrometer for High Resolution Gas Phase UV Photoelectron, Auger Electron and Ion Fragment Spectroscopy.** P. Baltzer, B. Wannberg and M. Carlsson Göthe. UUIP-1182, 1989. Accepted for publication in Rev. Sci. Instr.
II	**An easy to build, high intensity monochromator for Helium II radiation applied to inner valence photoelectron studies of small molecules.** P. Baltzer, M. Carlsson Göthe, B. Wannberg and L. Karlsson. UUIP-1228, 1990. Submitted to Rev. Sci. Instr.
III	**Doppler free energy release spectroscopy.** P. Baltzer, M. Carlsson Göthe, B. Wannberg and L. Karlsson. UUIP-1231, 1990.
IV	**A Data Acquisition and Information Handling System in Ada for Electron Spectroscopy.** M. Carlsson and L. Asplund. UUIP-1165, 1987. Ada Letters 1988.
V	**Integrated Charge Sensitive Electron Detector for Electron Spectroscopy.** M. Carlsson, L. Asplund, C-J Fridén and M. Lundquist. UUIP-1166, 1987.
VI	**The Distributed Ada Run Time System, DARTS.** M. Carlsson Göthe, D. Wengelin and L. Asplund. Submitted to Software, practice and experience.
VII	**A System Structure to Avoid Busy Wait.** D. Wengelin, M. Carlsson Göthe and L. Asplund. Ada Letters, vol 10, no 1, 1990.
VIII	**Real Time Ada Compilers for the 68020.** L. Asplund, M Carlsson Göthe, D. Wengelin and G. Bray. Ada Letters, vol 9, no 7, 1989.
IX	**Analysis of experimental spectra using spreadsheets.** M. Carlsson Göthe, L. Karlsson, J. de Sousa Pires and S. Svensson. UUIP-1237, 1990. Submitted to Computers in Physics.
X	**High resolution, monochromatized HeIIα excited photoelectron spectrum of the 5s correlation satellites in Xe.** M. Carlsson Göthe, P. Baltzer and B. Wannberg. UUIP-1232, 1990.

XI	**High resolution, monochromatized HeIIα excited, photoelectron spectra of N_2, CO and O_2.** M. Carlsson Göthe, P. Baltzer, L. Karlsson, B. Wannberg and S. Svensson. UUIP-1233, 1990.
XII	**Inner Valence Satellite Structure in High Resolution X-ray Excited Photoelectron Spectra of N_2 and CO.** S. Svensson, M. Carlsson Göthe, L. Karlsson, A. Nilsson, N. Mårtensson and U. Gelius. UUIP-1200, 1989. Submitted to Chem. Phys.
XIII	**X-ray photoelectron, Auger electron and ion fragment spectra of O_2 and potential curves of O_2^{2+}.** M. Larsson, P. Baltzer, S. Svensson, B. Wannberg, N. Mårtensson, A. Naves de Brito, N. Correia, M. P. Keane, M. Carlsson Göthe and L. Karlsson. J. Phys. B **23**, 1175 (1990)
XIV	**The NVV Auger electron spectrum of the HI molecule.** L. Karlsson, S. Svensson, P. Baltzer, M. Carlsson Göthe, M. P. Keane, A. Naves de Brito, N. Correia and B. Wannberg. J. Phys. B **22**, 3001 (1989).
XV	**Vibrationally Resolved Study of the Fourth Photoelectron Band of Acetylene at 23.5 eV.** M. Carlsson Göthe, F.T. Chau, P. Baltzer, S. Svensson, B. Wannberg and L. Karlsson Accepted for publication in Chem.Phys.Lett, 1990.
XVI	**X-ray, UV and synchrotron radiation excited inner-valence photoelectron spectra of CH_4.** M. Carlsson Göthe, B. Wannberg, L. Karlsson, S. Svensson, P. Baltzer, F. T. Chau and M-Y Adam. Accepted for publication in J. Chem. Phys 1990.
XVII	**A high resolution HeI excited photoelectron spectrum of the H_2CO molecule.** M. Carlsson Göthe and L. Karlsson. UUIP-1234, 1990.
XVIII	**Effects of relaxation and hyperconjugation on shake-up transitions in X-ray excited photoelectron spectra of some small carbonyl compounds.** M. P. Keane, S. Lunell, A.Naves de Brito, M. Carlsson Göthe, S. Svensson, B. Wannberg and L. Karlsson. UUIP-1235, 1990.
XIX	**Observations of a barrier and a double well in the potential curve of the C-state of the CO^+ molecule.** M. Carlsson Göthe, B. Wannberg , L. Karlsson, S. Svensson and P. Baltzer. Uppsala University Internal Report, UUIP-1236, 1990.

References to these papers will be written in roman numerals.

2. CONTENTS

3. INTRODUCTION

Experimental physics is, in principle, just the "simple" process of performing measurements on a physical system and interpreting the results. These observations will then verify or falsify the physical models used to describe the system and to predict the observations. The schematic drawing in figure 1 shows this process. In reality this is not a simple task. In the case of instrumentation, several factors have to be taken into consideration. First, the experiment must be carried out under such conditions that the instrument interacts with the system under investigation in a controlled manner. The desired interactions must be enhanced as much as possible while all unwanted interactions must be suppressed. For instance, if we want to illuminate a sample with radiation of a well known energy, all other radiation energies should ideally be removed. Second, the actual measurement method must not disturb the system. Third, the measured data have to be collected and stored with the same or higher speed that they are produced. The data must not be distorted in this process. As regards interpretation of the results, this part of the work is largely based on experience and comparison with applications in the same field and related fields, calculations and simulations of suitable models of the physical system under investigation, and finally trial and error.

This thesis shows several examples of the interaction between experiments and theory shown in figure 1. For example, the possibility to analyze ion fragments in the electron spectrometer (Paper I) resulted in a number of photoelectron and ion fragment studies presented in ref. [1] and in Paper XIII. In the study of the dissociation processes in ionized O_2, described in Paper XIII, both singly and double charged ions were detected. Using only the photoelectron spectrometer it was not possible to separate these processes. This was one of the incitements for the development of new instrumentation for ion fragment studies described in Paper III.

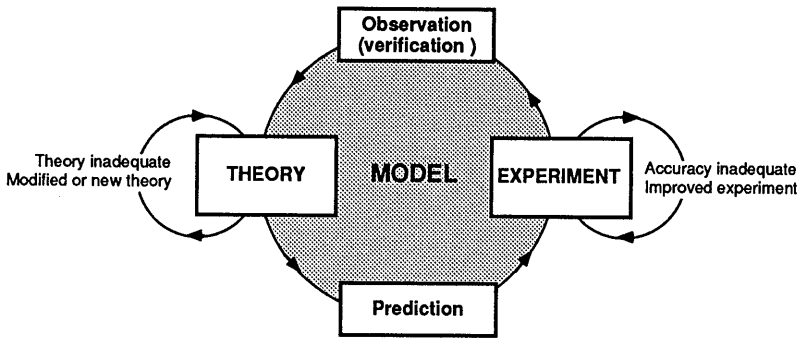

Figure 1. The interaction between experiments and theory.

Another example is the development of the monochromator for HeIIα radiation, described in Paper II. This device has made high resolution studies of the inner valence region of N_2, O_2 and CO possible. The studies have given an increased knowledge of the dynamics of these molecules. An anomalous vibrational structure observed in the $C\ ^2\Sigma^+$ band of CO^+ (Paper XIX) was used in the revision of the potential curve model for this state. However, in order to increase the knowledge of the inner valence region even more, the resolution of the spectrometer has to be improved. Also, other types of experiments, *e.g.* mass spectroscopy on dissociation fragments, may further improve the models used for the potential curves of CO^+.

One design idea that has been prevalent in the group for the last years is the one advocated by Dr. P. Baltzer. It stresses the need for including suitable provisions for adjustments and diagnostics in the experimental equipment. Such a design idea influences both the mechanical design and the design of the data acquisition system. A proper mechanical design relaxes the demands on manufacturing accuracy. The data acquisition system must then aid in the adjustments and diagnostics of the experiment. The spectrometer described in Paper I and the monochromator described in Paper II are examples of this approach.

4. INSTRUMENTAL DEVELOPMENT

4.1. The Electron Spectrometer

Extensive modifications of an electrostatic electron spectrometer of the hemispherical type have been performed and are described in Paper I. This work has been summarized in two sentences that I would like to quote; "The paper describes a major reconstruction of an old multi-purpose electron spectrometer into a dedicated gas phase high resolution instrument. The main features of the instrument are ease of operation and adjustment." [1]. This is indeed an excellent description. The original instrument was designed to be ultra high vacuum (UHV) compatible. This required metal seals on all flanges and numerous bolts, which resulted in laborious mounting and dismounting of the spectrometer. As the instrument is used for high resolution gas phase studies, the access to the interior of the spectrometer is essential to maintain the high resolution. Dismounting and mounting of the excitation source, the gas cell and the lens may now be performed in only a few minutes which results in an operational instrument after about 15-30 min of pumping. This ease of use was essential when iterative improvements were carried out to the instrument, *e.g.* the signal to background reduction described in Paper II.

The spectrometer has been modified in two additional steps after the major modification discussed above. Revisions of the excitation compartment and the multichannel detector were necessary to adapt the spectrometer for the ion coincidence experiment described below. The new compartment interfaces uniformly to all excitation sources used; the electron gun used in ion fragment and Auger electron spectroscopy, and also the ECR lamp and the HeII monochromator used in photoelectron spectroscopy. Furthermore, a new gas cell with differential pumping has recently been designed. The latter redesign was necessary to reduce the background at low kinetic energies of the spectra recorded

with monochromatized HeIIα radiation and to reduce the gas load in the analyzer compartment. This spectrometer, which has been used in most of the experimental studies in this thesis, is shown in figure 2.

The highest resolution recently obtained with the new gas cell arrangement, using HeIα radiation, is 10 meV (FWHM) for the Xe $5p_{3/2}$ line, at 5 eV pass energy in the analyzer, *cf* figure 3.

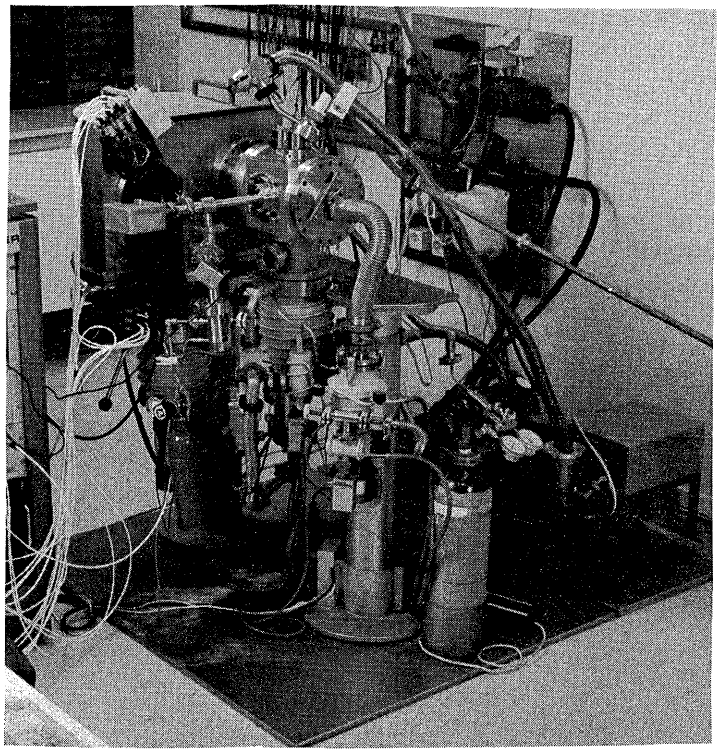

Figure 2. *The electron spectrometer.*

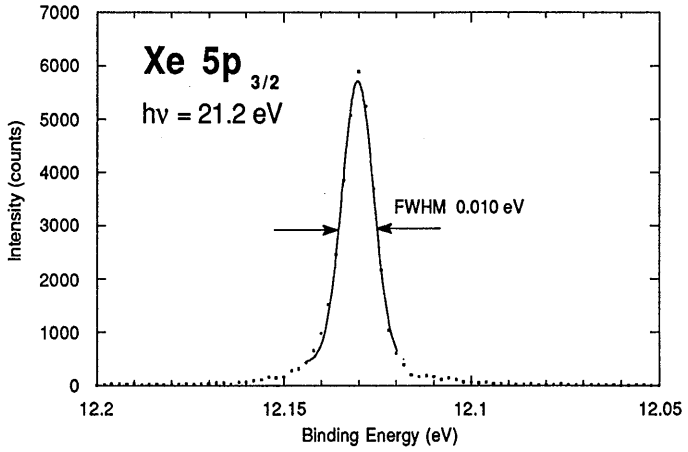

Figure 3. *A photoelectron spectrum of the Xe $5p_{3/2}$ line excited by HeIα radiation.*

4.2. The Monochromator

The possibility to perform inner valence studies with high resolution using monochromatized HeIIα radiation has been discussed for a long time. I can only speculate why such an instrumentation has not been implemented earlier for gas phase studies. One reason may be that intense HeII sources have not been available. This would then result in an unacceptable intensity loss in the monochromatization of the radiation, resulting in a poor signal to noise ratio or very long times for data collection. The microwave ECR lamp used in all photoelectron studies included in this thesis is at least one order of magnitude more intense compared to previously used HeI and HeII sources. Furthermore, the use of a double focusing toroidal grating gives only a small reduction of the HeIIα radiation intensity. As the width of the helium lines is small (≤4meV) [2], compared to the spectrometer resolution (≥10meV), low requirements are put on the resolution of the monochromator. The purpose with the present design was only to reduce the HeI intensity. A schematic drawing of the monochromator is shown in figure 4. A full description is given in Paper II.

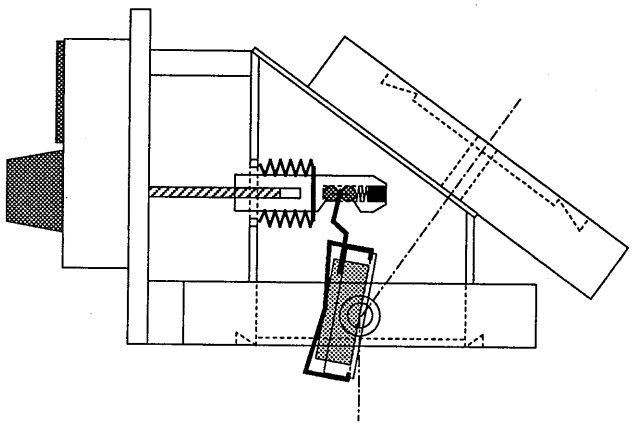

Figure 4. A schematic drawing of the HeII monochromator.

The design principle of including suitable provisions for adjustments while relaxing the demands on mechanical manufacturing tolerances is to a high degree followed in this work. It was found, and proven by ray tracing calculations, that only two degrees of freedom were necessary for monochromator alignment and wavelength adjustment. This radically simplifies the design, manufacturing and usage of the unit.

The monochromator has been used in studies of the 5s correlation satellites of Xe presented in Paper X, the inner valence region studies of the N_2, O_2 and CO molecules presented in Papers XI and XIX, and in the inner valence study of CH_4 presented in Paper XVI. The performance tests show that the usable binding energy region has been extended from 26 eV, using unmonochromatized HeII radiation, up to almost 40 eV when using the monochromator.

4.3. The Ion Coincidence Experiment

A new method for measurement of kinetic energy release in the dissociation of doubly ionized free molecules has been developed and is presented in Paper III. The thermal motion of the dissociating molecule is measured and corrected for, thus giving a Doppler free spectrum. This gives a significant improvement in the resolution since the major broadening in the ion fragment spectra is due to this effect. For a molecule dissociating into two fragments of masses m_A and m_B with a total energy release of E_F at the temperature T, the FWHM of the Doppler profile is

$$\frac{4}{m_A+m_B}\sqrt{ln\,2\,m_A\,m_B\,E_F\,kT}$$

When $m_A=m_B$ the worst case appears, resulting in a broadening of 0.86 eV at E_F=10 eV and T=300 K. This corresponds well to the observations made in the study of dissociation ion fragments of O_2^{++} presented in Paper XIII.

To determine the actual energy released in the dissociation, regardless of the thermal energy of the initial molecule, the energies of both fragments were measured using a coincidence arrangement. The spectrometer, presented in Paper I, was modified for this purpose. Since a continuous electron gun was used for excitation no direct time reference was available. The hemispherical analyzer was used to measure the energy of one of the fragments. A simple time-of-flight drift tube, equipped with a channeltron, was used in the opposite direction to detect the other fragment. Only charged ion fragments may be detected. Therefore, all dissociation processes resulting from singly charged molecules are suppressed.

The ions detected in the spectrometer channel possess a well defined energy and thus their flight time may be calculated and used as a time base for the other channel. The directly measured quantity is the time difference between the two fragments.. A coincidence time window is calculated with a position relative to events in the spectrometer channel. If an event in the time-of-flight appear within the coincidence window this is regarded as a real coincidence. The time difference used for energy correction is measured to much higher accuracy than the width of the coincidence window. The size of the window can be chosen to optimize the ratio between real and random coincidences. The coincidence controller program has been designed to minimize the energy correction calculations.

Performance tests have been made on the H_2, D_2, HD and O_2 molecules and these results are presented in Paper III. The tests suffered from rather long measurement times. The recording time of the O_2 spectrum was approximately one week with an overall count rate of 0.05 counts/s. The paper suggests that further development of the instrumentation can be done in order to improve the resolution and in particular the count rate of the experiment.

5. MEASUREMENT AND DATA ACQUISITION

The Measurement and Data Acquisition group at the Department of Physics in Uppsala, active from 1984 to 1990, has been working with transducers, communication, computer software and computer hardware. These are the four main components in data acquisition systems, which forms the link between the experiment and the resulting data. Measurement and Data Acquisition is thus an integral part of experimental physics.

The success of the experiment is often depending on the transducer. Communication links and computers are only transporting, storing, analysing, and presenting the experimental data. However, these areas can not be neglected as the data must not be distorted. Also, when using a number of computers in the life-cycle of a set of data, *e.g.* a spectrum, simple intercomputer transfer routines are essential.

The group has in the last two years concentrated its interest in the area of distributed systems. This is so because scientific, real time, data acquisition and control systems are often built as distributed, multi-processor computer systems. High fault tolerance is often required in scientific systems. The design and implementation are often complex due to a distributed hardware configuration. By adding a uniform run time support for distributed scientific applications, most of these difficulties may be solved. The gain is large when using a distributed configuration. Not only is it possible to increase the performance of the system, but a natural redundancy is included.

5.1. Ada in scientific software.

The Ada programming language was developed on initiative of the US Department of Defence. It is a general language with large possibilities to design elaborate data- and program structures although it was primary intended as a programming language for real time embedded systems, *i.e.* systems where the software is a component just as the electronics and the mechanics. Such systems often consist of several concurrently executing modules. Operating system facilities are normally used for communication and synchronization between such modules. These calls are specific to each OS and therefore result in unportable systems. With Ada, parallel processes, communication, and synchronization are included in the language. Such parallel processes, named *tasks*, may be both statically or dynamically created, and may be included in other data type structures. These parallel processes are particularly useful in scientific data acquisition and control systems. In such systems, parallel units or activities in the real world may be coded as tasks. This simplifies the coding and enhances the readability and the reliability. As stated above, tasks are concurrently executing code modules. This may be true for a multi-processor system, but for a single processor system the execution of the tasks is in some way time sliced. The selection of tasks for execution is determined by priorities.

One of the main purposes in the creation of Ada was to promote portability of application software between various target systems. This has been, in my and others opinion, one of Ada's weakest points. The two key features in Ada that were meant to improve

portability were a unified mechanism for parallel processing, as mentioned above, and possibilities to direct the layout and representation of the data structures. The latter would eliminate the need for data conversion routines and drivers, often written in assembly language, to interface to memory mapped IO devices. However, none of these features has been totally accepted, although for different reasons. The tasking, generic, and exception mechanisms in Ada have not been generally accepted by the software producers. This is, primarily, due to the impossibility to prove that the exact behaviour of systems using these mechanisms is correct. Also, the rendezvous times, i.e. the time to transfer the control from one task to another, have previously not been short enough to satisfy the response requirement in real-time systems. The second key feature has failed due to the freedom given to the compiler vendors as a number of 'implementation dependent' items in chapter 13 of the LRM [3]. If the use of Ada in scientific systems is based on the promise of easy portability and low level description of data structures, it is essential to test this in reality.

The issues of portability and efficiency were investigated in Paper VIII. Three compilers for the same host and target systems are evaluated. It may be noted that none of the three compilers has a uniform interpretation of how an address constant should be expressed. The same divergence is found when linking an interrupt to a task. But even worse, the Alsys Corp. compiler required an elaborate assembly code driver to interface the interrupt handler task. However, when designing a system is it essential to use the tools for data abstraction and information hiding given in the Ada language. This concentrates the unportable features in embedded structures and packages and restricts their spreading over the massive application code. Porting the system then requires modifications of only these structures and packages. It may be concluded that Ada probably gives better support to the application programmer than any other language. However, in the main issues, low level control and timing requirements, Ada is still weak.

5.2. Data acquisition systems

The area of data acquisition and control systems has, along with the mechanical and electrical components, become an integral part of experimental physics. This is due to the high data flow, long measurement times, requirements on data precision, and the enormous numbers of data values. Only electronic systems such as computers are possible in assisting an experimental physicist in these tasks.

A data acquisition and control system consists of several parts. The control system is often separated from the data acquisition system, but with remaining links for user status and control information [4]. The remaining components in the data acquisition system are then:

- The transducers and other peripherals with their software interfaces.
- Data collection routines.
- The users experimental description and data presentation routines.
- Data storage and retrieval abilities.

Often, software for optimization of experimental parameters given as integrated software components or as stand alone programs, is essential in the experimental work.

Two systems for data acquisition are presented in this thesis. The first one, described in Paper IV, is a major prototype for a data acquisition and control system for electron spectroscopy. The second one, described in Paper III, is a data acquisition system for coincidence measurement of ion fragments. The usefulness of Ada in scientific systems, such as data acquisition and information handling systems, has been evaluated. The experience gained from these studies is presented in Papers III and IV.

The EDIS, Esca Data Acquisition and Information Handling System, was intended as an replacement for the existing Nuclear Data 6600 system used in the laboratory in 1987. The system was completed to a prototype level with full functionality in most components. The system was hosted and targeted for a μVAX II running VAX/VMS with a double channel IEEE-488 instrument bus and serial ports used for spectrometer communication. The system was intended to serve at least two spectrometers and utilise multiterminal usage. The system was written in Ada and compiled using the DEC ADA compiler version 1.3 .

The coincidence data acquisition system, described in Paper III, was built just like the mechanics and the electronics, as a supplement to the existing electron spectrometer system presented in Paper I. The coincidence control system was developed in Pascal and run on a Macintosh Plus computer. The user interface was designed by using the Prototyper automatic code generator for the Macintosh. The configuration of the system is shown in figure 5.

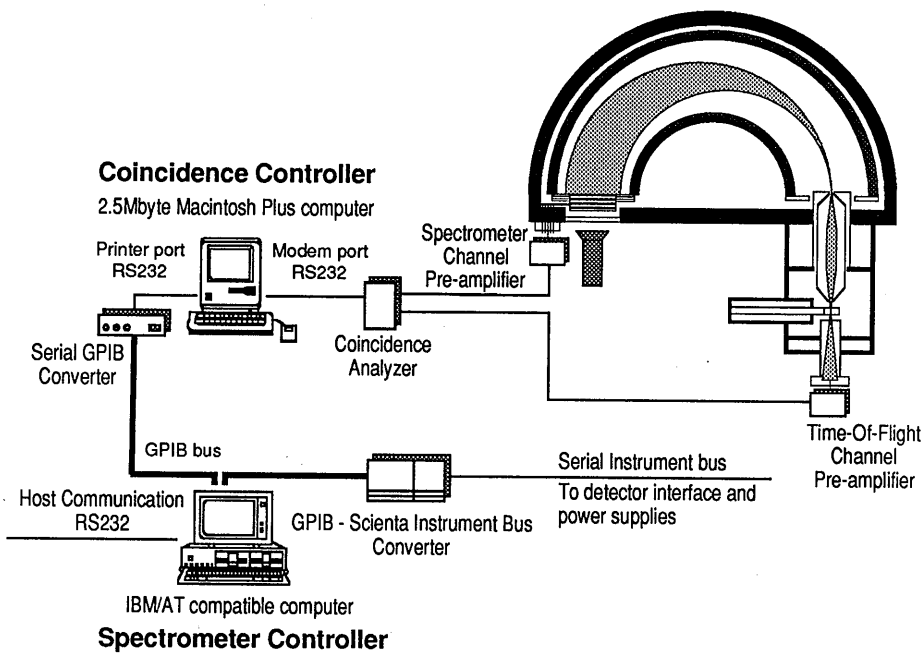

Figure 5. A system diagram of the coincidence experiment.

One of the difficulties in the latter system was to reduce the computing load on the coincidence control program. This reduction was necessary to maintain a rapid response to user interactions, while keeping up with the production of coincidence data pairs. The obvious solution was to introduce a dedicated data reduction unit between the pre-amplifiers and the coincidence control program. This unit was designed using hardware FIFO buffers to allow data bursts and was programmed in assembly language to allow for high speed data processing while maintaining the algorithmic flexibility of computer software. It was found in performance tests that the unit could handle 1 K events/s before saturation. At this data rate, typically only 0.05-1 events/s were associated with true coincidence events and sent to the coincidence control program.

Only minor modifications were made to the original spectrometer data acquisition program. The coincidence control system was added, as a listener, to the GPIB IEEE-488 bus used for instrument communication. A set of GPIB commands were used in the communication between the two computer systems.

5.3. Distributed systems

There are in principle two ways to improve the performance of a computer system. The first is to increase the computing power by faster processors and hardware support like numerical coprocessors. The other is to connect a number of processors, or complete computers, together on a common bus or in some network. The multiprocessor solution does not only increase the computing performance, but also increases the fault tolerance of the whole system. This is due to the fact that the remaining processors may continue their service even if one of the processors fails. A system composed of several computers as described above is often named a *distributed system.* Making an application program to run on a distributed system is however more complicated than in the single processor case. In recent years, much effort has ben put into the area of using Ada on distributed target systems.

Two major hardware configuration categories exist in the field of distributed systems; tightly coupled and loosely coupled. In a tightly coupled system the processors share a common memory through which communication and synchronization may be performed. In a loosely coupled system the computers, named *nodes*, are interconnected in some network. All interprocessor communication is performed over this network. A number of compiler vendors offer solutions for tightly coupled systems. In the loosely coupled area the situation is different. Intense research during the last years has resulted in an number of projects [5,6,7].

Somewhere in the realization of a distributed application, a decision has to be taken of how to split the software components over the nodes. The decision can be taken early, in the *design and code phase*, and entered into the source code. This method is called pre-partitioning. The choice can, on the other hand, be taken as late as possible, in the *integration phase.* This method is called post-partitioning. Several pros and cons can be noted on either solution [8,9]. Not only is there a debate about how and when the partition should take place, but also about which software components should be dis-

tributable. Four alternatives are reported in the literature; on Ada programs, on tasks, on packages, or on any part of an Ada program. The LRM [3] gives no guidance but mentions briefly, in section 9(5), that tasks may execute in a multicomputer environment. No mechanisms are included in the language to assign tasks, or any other software parts, to a particular processor in a distributed system. Neither does the LRM define the state of the program after the loss of a part of the computing environment, *e.g.* a processor.

DARTS, the Distributed Ada Run Time System presented in Paper V, is developed by the Measurement and Data Acquisition group, in collaboration with the Swedish Defence Research Establishment. The system is mainly a run time base for distributed applications and is implemented fully in Ada. It also defines rules for transforming an application to interface to the distributed system. The intentions with the system are to test Ada in real time applications and to create a test-bed for distributed applications, *e.g.* scientific systems.

DARTS also implements a number of special features not commonly found in distributed solutions. When studying the functionality of related systems, *e.g.* DEC Net and LocalTalk, I found that these do not require such a static behaviour as most distributed systems do. Most communication networks allow nodes to enter and leave the network naturally. When a node signals its appearance in the network, it logs-on by telling the other nodes its 'name and number'. The nodes signal that they are still hooked-up by sending small messages saying 'I am alive'. This method is called *heart-beating*. No node knows in advance which nodes will appear on the network. This was the kind of functionality I wanted to introduce in DARTS and it was found to give a number of spin-off advantages.

In DARTS, I selected the distributable software components to be tasks, task types, packages, subprograms, and variables. These components are referred to as *distributed units, DU*. One may now be interested to know how the distribution information may be expressed, and entered into the Ada application code, when we know little of the number of nodes that will execute the program. This is done using a two step method. As the first step, I used two pragmas, *i.e.* compiler or pre-processor instructions, to bind a distributed unit to a virtual node (VN). The first pragma DISTRIBUTE enumerates the VNs on which a software component should execute. The second pragma REDISTRIBUTE enumerates the VNs on which the component might execute if the host is lost due to a node failure. These two pragmas fully control the source code transformation that interfaces the application code to the underlying distributed run time system. The second step binds a virtual node to a physical node (PN) and a configuration information file is generated for each PN, including a unique node number. The configuration information is read by each node at start-up and is used to elaborate the proper software components of that node. Now, several physical nodes may host copies of the same virtual node. When a new node notifies its existence on the network, the new and the old nodes interchange configuration reports informing about their hosted DUs. The node and DU information is kept in data bases.

Note that the pragma DISTRIBUTE might enumerate a number of nodes for each DU. This implies that packages, subprograms, and variables are executing on several nodes. A calling node will determine, *e.g.* according to load, which node to call. In the case of task objects, the node list will indicate the possible nodes for object creation. The pragma DISTRIBUTE also takes another parameter, distribution criterion, defining how to select among the possible nodes. A task type, selected for distribution, might be given AVERAGE_LOAD as the distribution criterion along with its node list. When a task is created from this type, the node in the list presently having the lowest load will be commanded to create and host the new task object.

DARTS as it has been described above may be regarded as a pre-partitioning system. However, it may also be used for postpartitioning. This is possible since the configuration information, mentioned above, is kept in a file, unique for each node. In this file the node name, all DUs and their states are listed. The DUs may be assigned to LOCAL, REMOTE, or REMOTE_AND_IDLE states. By editing these states the configuration may be changed between system restarts without recompilation. The node list in the pragma DISTRIBUTE may now be interpreted as the first iteration of where the units are to be distributed for executing. The union of the node lists, in the DISTRIBUTE and REDISTRIBUTE pragmas, are the nodes that have the potential to host the DU.

With the functionality of DARTS in mind, redistribution now follows without any further complexity. Node failures are detected by the loss of heartbeat signals from a node. The redistribution is simply performed by extracting a list of the lost DUs from the unit data base. For each DU a target node is selected and an initiation command is sent to the target node. The node and unit data bases are updated on all reminding nodes.

In the implementation of distributed systems one sometimes has problems of putting an inactive caller in a hibernating state during a call to a remote node [10]. This results in busy waits which reduces the performance of the system. We have reported in Paper VI that this is not the case in DARTS. The use of two sets of agents eliminates the need of busy waits.

6. EXPERIMENTAL APPLICATIONS IN CHARGED PARTICLE SPECTROSCOPY OF ATOMS AND SMALL MOLECULES.

The following section summarizes the various charged particle studies performed using the experimental equipment described in Papers I, II and III. The term charged particle spectroscopy summarizes a number of experimental methods. In this thesis four different methods are used; photoelectron spectroscopy using various excitation energies, Auger electron spectroscopy, ion fragment spectroscopy, and ion coincidence spectroscopy.

In the photoabsorption process the atom, or molecule, is excited by a photon of energy $h\nu$. If this energy is larger than the binding energy E_b of the electron photoionization may occur. The electron leaves the atom or molecule with a kinetic energy of $E_k = h\nu - E_b$, *cf* Figure 6. This is referred to as the photoelectric effect. The ejection of a photoelectron

may be accompanied by excitation in the ionic system, referred to as shake-up and shake-off processes. These processes give rise to satellite lines in the spectrum which provides very useful information about the electronic structure of the system and of the photoionization process. All these processes are primary processes starting with an atom or molecule in its ground state, in the conventional photoelectron spectroscopy experiment.

The Auger and autoionization are, on the other hand, both secondary decay processes, starting with an atom or molecule in an excited state. In the Auger process the excited ion is initially created by the removal of a core electron by means of electron or photon impact. The core hole **i** may now be filled from another shell **j** leading to the emission of an electron from some shell **k**. This notation is used when classifying the **ijk** Auger lines. In the autoionization process the initial state is an excited state in a neutral atom or molecule. If the energy released in the following deexcitation is sufficient, the system can rearrange to an ion by the emission of an electron. These two processes can give rise to intense lines in electron spectra and are shown schematically in Figure 6.

In the case of molecules, the excited or ionized system may dissociate into smaller fragments. This is possible if the molecule is excited into a repulsive state, through tunneling in a predissociative state or if the excitation energy exceeds the dissociation limit of a bound state.

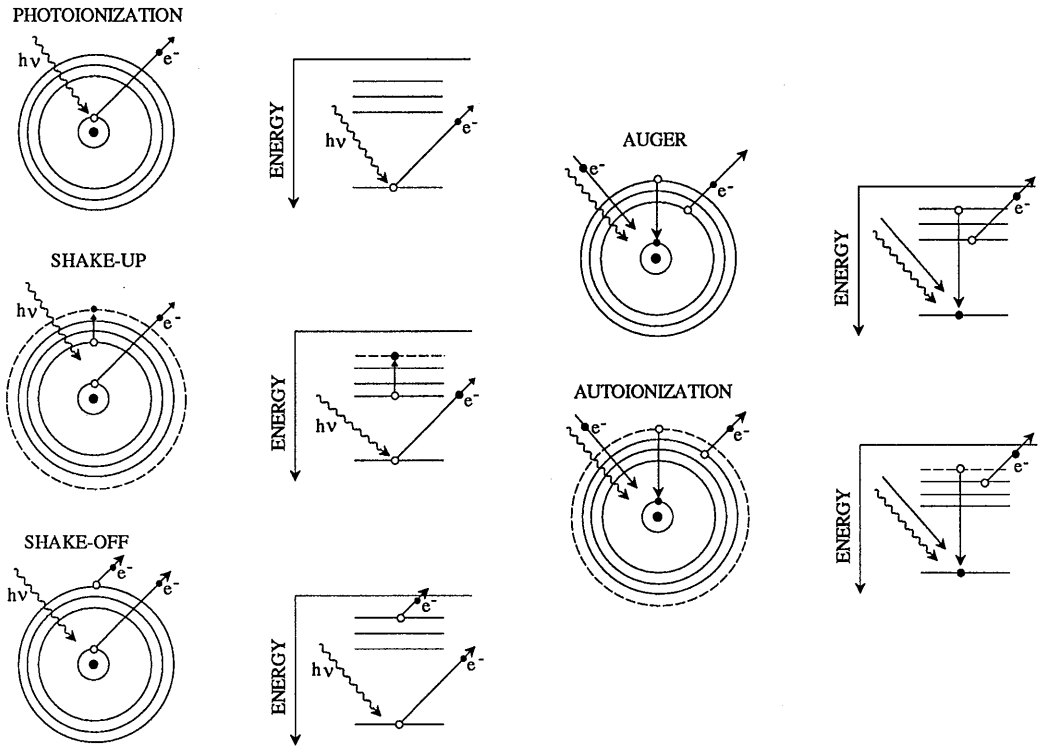

Figure 6. *The electron emission processes.*

6.1. Inner valence study of the 5s correlation satellites in Xe.

The inner valence region of Xe has earlier been investigated using ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) as well as synchrotron radiation photoelectron spectroscopy (SRPS). In the previous works both the resolution and the signal-to-noise ratio have been comparatively low. Therefore, only limited information of the 5s correlation satellites region has been available. From SRPS studies it is known that some of the lines in this region show strong energy dependence [11]. Especially the $(^1D)5d\ ^2D_{3/2}$ line at 27.942 eV and the $(^1D)5d\ ^2S_{1/2}$ line at 28.876 eV showed an increasing intensity with increasing photon energy.

In the present study, approximately 70 new lines, previously not observed in photoelectron spectroscopy, are identified. These lines correspond well to the optical data given by Morse [12] and by Hansen and Persson [13,14]. It may be noted that strong lines were observed in the spectrum which must be associated with levels of high angular momentum. One example is the $(^1D)5d\ ^2G_{9/2,7/2}$ levels at 26.337 eV with a relative intensity of 12% of the main 5s line. A detail of the Xe spectrum is shown in figure 7.

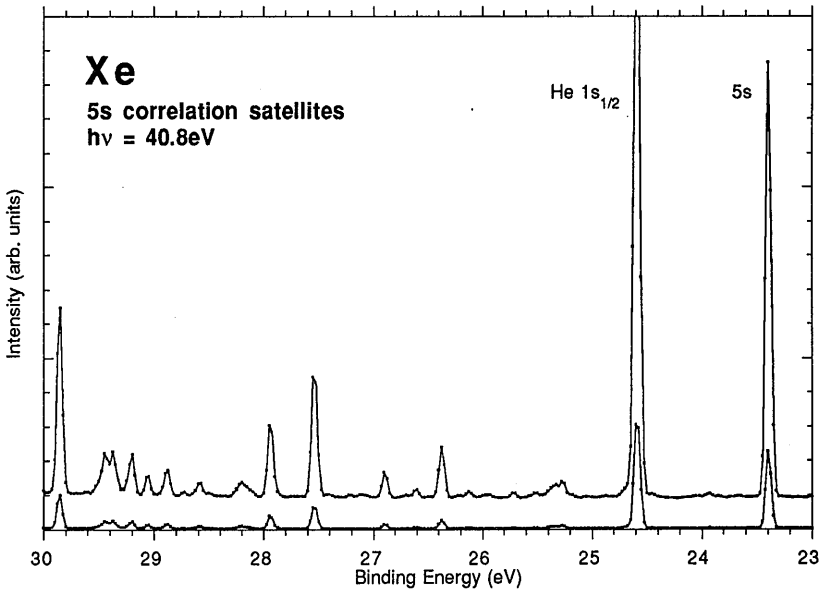

Figure 7. *The high resolution photoelectron spectrum of the 5s correlation satellites in Xe.*

6.2. Inner valence studies of N_2, CO and O_2.

New high resolution spectra of N_2, CO and O_2 are presented in Papers XI, XII and XIX. By comparing newly recorded X-ray spectra, resonance Auger spectra (DES) and monochromatized HeIIα excited spectra, a new state designation has been outlined for N_2 and CO. In the inner valence region a number of new states have been observed.

The high resolution studies of these small molecules, which in many cases reveal long vibrational progressions, have enabled the calculation of potential curves for the corresponding cationic states. The Morse potential curves for CO^+ are shown in figure 8. In the case of the C $^2\Sigma^+$ state two regions with completely different vibrational spacings are observed. This behaviour has been interpreted as caused by a double potential well, *cf* figure 8, as described in Paper XIX.

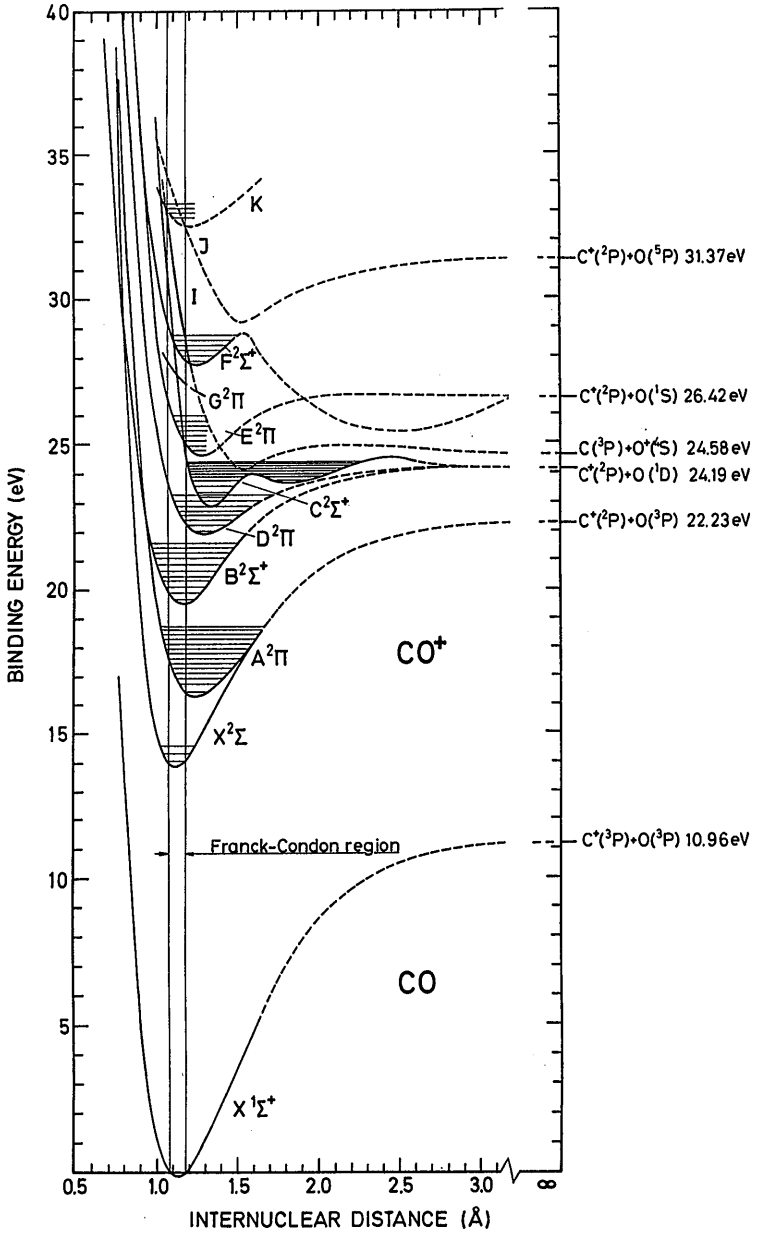

Figure 8. *The Morse potential curves for CO^+ obtained in Paper XIX.*

The O_2^{2+} ion has been studied in Paper XIII. The investigation was performed by means of electron impact induced and photon induced Auger electron spectroscopy and ion fragment spectroscopy. Potential energy curves for a number of electronic states of the O_2^{2+} were calculated. It was found that the Doppler broadening in the ion fragment spectrum smeared out any vibrational structure possibly present in the spectrum. This initiated the introduction of the coincidence ion fragment spectroscopy experiment and the study of O_2^{2+} by this technique.

6.3. HI

The electron beam excited NVV Auger electron spectrum of HI is presented in Paper XIV, together with a new recording of the X-ray excited spectrum of the I4d core lines. It is shown that the initial I 4d core hole state is vibrationally excited. The Auger spectrum of HI shows vibrational excitations in the doubly ionized π^{-2} states. Also, relativistic effects are seen to be important.

6.4. Inner valence study of Acetylene.

The inner valence C $^2\Sigma^+_g$ electronic state of the acetylene cation has been studied by means of HeIIα excited UV photoelectron spectroscopy. The vibrational structure of the band is resolved and interpreted in terms of a vibrational progression in the totally symmetric $\nu_2(\sigma^+_g)$ mode. A Franck-Condon analysis has been carried out and force constants $F_s(1,1)$, $F_s(2,2)$ and $F_s(1,2)$ were determined. These force constants correspond to the CH stretching, CC stretching and CH-CC stretching interactions, respectively. The CH and CC bond lengths have been deduced and the values are found to be 1.088 ± 0.005 Å and 1.439 ± 0.005 Å, respectively. These values are considerably larger than the bond distances of the neutral ground state (1.058 and 1.208 Å). This is in accordance with calculations assigning CH and CC bonding character to the $2\sigma_g$ orbital. Removal of an electron from the orbital weakens both the CH and CC bonds to different extents, resulting in a lengthening of the bond distance.

6.5. Inner valence studies of methane.

The inner valence electronic states of the methane molecule have been studied by means of X-ray, synchrotron radiation and UV-photoelectron spectroscopy. This study is presented in Paper XVI. Extensive vibrational structures are observed in the $2a_1^{-1}\ ^2A_1$ state and a Franck-Condon analysis has been carried out, suggesting an equilibrium bond distance of 1.279 Å. The potential curve of the $2a_1^{-1}\ ^2A_1$ state has been calculated for methane by fitting a Morse potential to the observed vibrational energies. The vibrational lines have a Lorentzian shape and the line widths increase gradually. This probably indicates a short life-time of the vibrational states due to predissociation. A discussion of the potential curves related to the correlation satellites is included.

6.6. Outer valence study of formaldehyde.

The UV photoelectron spectrum of the outer valence region of formaldehyde is presented in Paper XVII. This study reveals, due to the high signal-to-noise ratio, extensive vibrational structure in the region between the X and the A band in the H_2CO-cation. This structure has been associated with excitations to various vibrational modes in the X state. The vibrational progressions acquiring the highest intensity are found to be the ν_3, $\nu_1+\nu_3$ and $\nu_2+\nu_3$, $2\nu_2+\nu_3$ and $\nu_1+\nu_2+n\nu_3$, *cf* Figure 9. The maximum intensity in the progressions was found at high vibrational quantum numbers. For instance, the $2\nu_2+\nu_3$ has its maximum at v=7 while the $\nu_1+\nu_3$ has its maximum at v=16. This might be associated with a shape resonance resulting in a broadening of the Franck-Condon region. These lines are expected to have a strong excitation energy dependence. Accordingly, the HeIIα excited spectrum, presented in Paper XVIII, does not show any of these structures. The same kind of structure was observed in the valence spectrum of CO^+ recorded by means of SRPS [15] and by HeI excitation [16]. The HeIIα excited spectrum of CO^+, presented in Paper XII, shows no evidence of any vibrational structure with high vibrational quantum numbers in the X band.

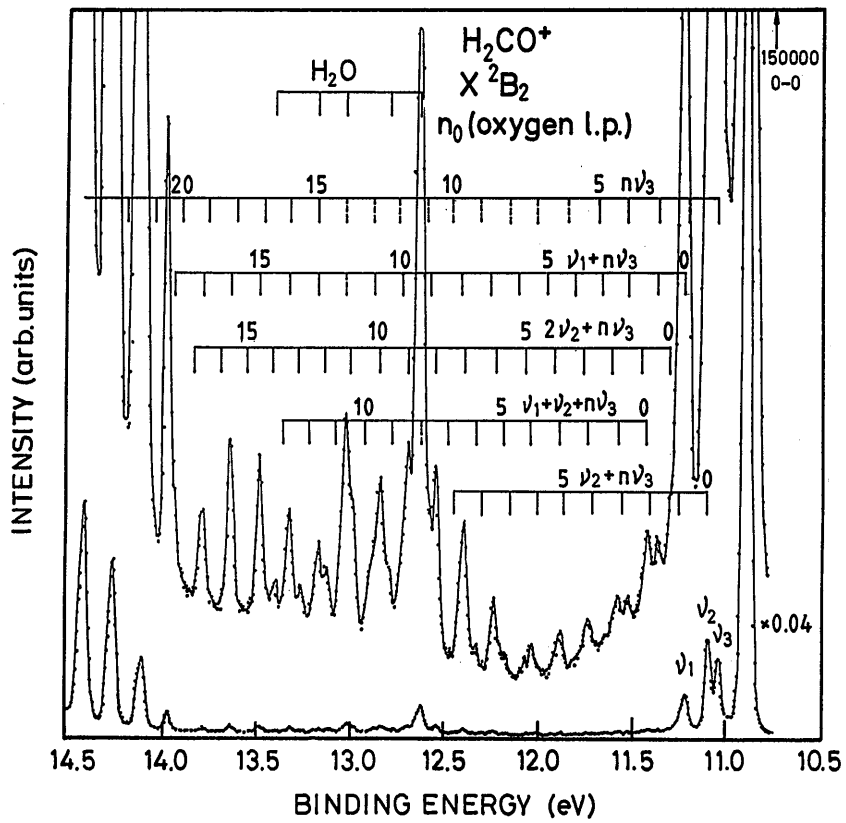

Figure 9. *A photoelectron spectrum of the X band in H_2CO^+ showing the extensive vibrational structure of the band.*

6.7. VII.Hyperconjugation interaction in formaldehyde, acetaldehyde and acetone.

The C1s and O1s core shake-up and HeII excited valence photoelectron spectra of formaldehyde, acetaldehyde and acetone have been studied and are assigned using INDO-CI calculations. It is found that the hyperconjugation interaction between the CH_3 π type orbitals and the C=O π orbital in the case of acetaldehyde and acetone is responsible for the large differences found in the shake-up spectra between formaldehyde on the one hand and the other two molecules on the other hand. The ionization from the 6a' σ_{C-O} orbital in acetone is found to give rise to a clearly observable vibrational progression whereas the corresponding orbital on formaldehyde is structureless. There is therefore a substantial stabilization of the bonds due to the methyl substitution.

7. ACKNOWLEDGMENTS

First of all, I would like to express my sincere gratitude to my supervisors over the years, Prof. Ulrik Gelius, Doc. Leif Karlsson and Doc. Lars Asplund. It has been most stimulating to work under their guidance.

I am also most grateful for the 10 years of solid friendship with Dr. Peter Baltzer. Without the efforts of him, Doc. Leif Karlsson, Doc. Björn Wannberg and Doc. Svante Svensson this work would have been impossible to accomplish.

The cooperation with the other members of both the electron spectroscopy group, the data acquisition research group and the group at the Swedish Defence Research Establishment (section 22) has been very stimulating. The skill of the technical staff including Jan-Olof Forsell, Lars Bolkegård, Tommy Andersson, Lennart Eriksson and Hans Rydåker is also greatly acknowledged.

Furthermore, I would like to send a special tanks to my lunch partners, Måns Lundquist and Björn Sundström. Without their and Jorge de Sousa Pires guidance in the Macintosh area the introduction to this high productivity tool would not have been so smooth. Thank you !

Finally, my deepest gratitude and love goes to my wife Britt-Louise for her never failing encouragement, support and patience. Also, I would like to thank my little daughter Hanna for not cheering me on to much during the completion of this thesis.

Mats Carlsson Göthe
Uppsala, October 1990.

8. REFERENCES

[1] P. Baltzer, thesis, Acta Univ. Ups. 197, Uppsala 1989.

[2] P. Baltzer and L.Karlsson,
Uppsala University Institute of Physics Report, UUIP-1211, 1989.

[3] *Reference Manual for the Ada Programming Language*,
(ANSI/MIL-STD-1815A), Ada Joint Program Office,
Department of Defence, Washington, D.C. 20301, 1983.

[4] U. Gelius, B. Wannberg, P. Baltzer, H. Fellner-Feldegg, G. Carlsson,
C-G Johansson, P. Münger and G. Vegerfors,
J. Electron Spectrosc. 52, 747, (1990).

[5] D. Cornhill, *Distributed Ada Project.* Honeywell,1982.

[6] C. Atkinson, T. Moreton and A. Natali,
Ada for Distributed Systems, Cambridge University Press, 1988.

[7] C. Atkinson, S. Goldsack, A. Di Maio and R. Bayan.
Journal of Object Oriented Programming, in print 1990.

[8] D. Cornhill, IEEE Computer Society Conference on Ada Applications and
Environments, 1984.

[9] T. Mudge, ACM, 5 , 64 (1987)

[10] G. Eisenhauer, R. Jha and J.M. Kamrad II,
Ada Letters, Vol 9, Number 2, 1989.

[11] C. E. Brion and A. O. Bawagan, J. Chem. Phys, in print 1989.

[12] C. E. Moore, Atomic energy levels, National Bureau Standards (U.S.) Circ.
No. 467, U.S. GPO, Washington, DC, 1949, Vol. 1.

[13] J. Hansen and W. Persson, Phys. Rev. A 18, 1459 (1978).

[14] J. Hansen and W. Persson, Physica Scripta 36, 602 (1987).

[15] L. Karlsson, S. Svensson and A. Svensson,
J. Phys. B, 22, 3423 (1989).

[16] B. Wannberg, D. Nordfors, K.L. Tan, L. Karlsson and L. Mattsson,
J. Electron Spectrosc. Rel. Phen. 47, 147 (1988).

9. PAPERS INCLUDED IN THESIS

9.1. Comments on my participation.

This thesis consists of three major parts; instrumental development, data acquisition system implementations and experimental applications. In the case of instrumental development, Papers I-III, the work has mainly been performed in collaboration with Dr. P. Baltzer and Doc. B Wannberg. In the case of the data acquisition systems, I have had the main responsibility in Papers III-VII. Furthermore, I am the designer of the DARTS system (VAX/ADA version) described in Papers VI-VII. In the case of experimental applications, I have contributed to the recording of the UPS spectra presented in Paper X-XVIII, including spectrometer operation, sample preparation and primary analysis of the spectra. I have had the main responsibility for the evaluation, spectrum fittings and interpretation in Papers X-XI, XVII and XIX. I have developed the computer tools for spectrum evaluation, fitting and interpretation described in Paper IX.

9.2. Abstracts

Paper I:

Optimization and Redesign of an Electron Spectrometer for High Resolution Gas Phase UV Photoelectron, Auger Electron and Ion Fragment Spectroscopy.

P. Baltzer, B. Wannberg and M. Carlsson Göthe.

Accepted for publication in Rev. Sci. Instr.

Abstract: Extensive modifications of an electrostatic electron spectrometer of the hemispherical type are described. The purpose of the modifications is to make the instrument more suitable for high resolution gas phase spectroscopy. The changes concern substitution of electrical adjustments for mechanical precision, improved flexibility in focusing and a new system of computer controlled power supplies and detector interface. The instrument is also used for energy analysis of positive ions. Conversion between positive and negative particle analysis is achieved simply by reversing the polarities of all relevant voltages by a number of switches. A gas cell with internal heating is described. The influence of gas cell conditions on resolution is shortly discussed. The computer programs used for spectrometer control, data acquisition, spectrometer optimization and calibration are described.

Paper II:

An easy to build, high intensity monochromator for Helium II radiation applied to inner valence photoelectron studies of small molecules.

P. Baltzer, M. Carlsson Göthe, B. Wannberg and L. Karlsson.

Uppsala University Institute of Physics Report, UUIP-1228, 1990.

Submitted to Rev. Sci. Instr.

Abstract: An easy to build, high intensity monochromator for helium II radiation is presented. The design includes a double focusing, non blazed, toroidal grating with a groove density of 800 l/mm. The adjustment and focusing properties of the design have been studied using an optical simulation program. It is found that all necessary adjustments of the grating may be performed by using only two degrees of freedom; rotation and sidewise shifting. Inner and outer valence photoelectron spectra of N_2 and CO have been recorded using monochromatized HeIIα radiation. The study reveals extensive vibrational structures in the inner valence region of both molecules. A new state has been identified in the CO molecule.

Paper III:

Doppler free energy release spectroscopy.
P. Baltzer, M. Carlsson Göthe, B. Wannberg and L. Karlsson.
Uppsala University Institute of Physics Report, UUIP-1231, 1990.

Abstract: A new method for measurement of kinetic energy release in the dissociation of doubly ionized free molecules is presented. The two fragments are detected in coincidence, and the thermal motion of the dissociating molecule is corrected for in real time by accurate measurement of the time difference between the fragments within the coincidence window. The low overall detection probability often encountered in coincidence experiments is avoided by taking advantage of the strongly peaked angular distribution from the two particle decay. Preliminary measurements on the doubly charged ions of O_2 and HD are presented. The experiments reported here constitute a feasibility study, and methods to enhance the information rate are discussed.

Paper IV:

A Data Acquisition and Information Handling System in Ada for Electron Spectroscopy.
M. Carlsson and L. Asplund.
Uppsala University Institute of Physics Report, UUIP-1165, Uppsala 1987.
Ada Letters 1988.

Abstract: A distributed, real time, data acquisition computer system for electron spectroscopy, ESCA, is presented. The design and implementation in Ada involves windowing, menues, forms, graphical presentation, multitasking and instrumental communication. Experiances using Ada is descussed. Ada has been used in all phases. Data types and packages are presented. It is found that the language is very suitable for scientific purposes.

Paper V:

Integrated Charge Sensitive Electron Detector for Electron Spectroscopy.
M. Carlsson, L. Asplund, C-J Fridén and M. Lundquist.
Uppsala University Institute of Physics Report, UUIP-1166, Uppsala 1987.

Abstract: A new integrated, charge sensitive, multi-detector is presented. The detector consists of metal charge collecting plates, high gain amplifiers, and coded readout electronics, all integrated on the same chip. Design, simulations and layouts are discussed. The sensitivity is 10^6 electrons and the space resolution is 0.15 mm.

Paper VI:

The Distributed Ada Run Time System, DARTS.
M. Carlsson Göthe, D. Wengelin and L. Asplund.
Submitted to Software, practice and experience.

Abstract: A distributed Ada run time system, DARTS, is presented. The system can be used in conjunction with a pre-partitioning as well as a post-partitioning paradigm. A single program can be partitioned to run on a loosely coupled multiprocessor system. The distributed units are tasks, task objects, packages, varables, procedures, and functons. Task objects can be dynamically distributed. High fault tolerance is assured by unit redistribution. Design decisions, implementation details and ideas are presented.

Paper VII:

A System Structure to Avoid Busy Wait.
D. Wengelin, M. Carlsson Göthe and L. Asplund.
Ada Letters, vol 10, no 1, 1990.

Abstract: Using a source code transformation approach to Ada in a distributed environment will give some implementation difficulties. This paper presentes an all Ada, portable, solution to the problem of suspending a caller on a node during a call to a remode node. This solution is based on two sets of tasks on each node, making it possible for a caller to hang on an entry during the call. Algorthms are presented in pseudo-Ada.

Paper VIII:

Real Time Ada Compilers for the 68020.
L. Asplund, M Carlsson Göthe, D. Wengelin and G. Bray.
Ada Letters, vol 9, no 7, 1989.

Abstract: Three cross compilers hosted on a VAX/VMS for the Motorola 68020 processor have been evaluated. The target machine, a VME system with a MVME133 processor card and a MVME340 digital IO-card, has been set up in an environment with a function generator and an oscilloscope in order to measure the ral time response. The compilers supply the run tile kernel. It is possible to use Ada for real time applications, with the use of optimization of accept statements task switch times can come down to the order of 15 - 20 μs.

Paper IX:

Analysis of experimental spectra using spreadsheets.
M. Carlsson Göthe, L. Karlsson, J. de Sousa Pires and S. Svensson.
Uppsala University Institute of Physics Report, UUIP-1237, 1990.
Submitted to Computers in Physics.

Abstract: Various steps in the analysis of experimental spectra are discussed. These procedures include data acquisition, pre-analysis, simulation, modelling and presentation. A dedicated pre-analysis program, called CrunchViewer, is presented. The usefulness of spreadsheet programs, here exemplified with Microsoft Excel for the Macintosh, in simulation and modelling is demonstrated in applications related to photoelectron spectroscopy of small molecules. An example of a photoelectron spectrum prepared for publication by these programs is given.

Paper X:

High resolution, monochromatized HeIIα excited photoelectron spectrum of the 5s correlation satellites in Xe.
M. Carlsson Göthe, P. Baltzer and B. Wannberg.
Uppsala University Institute of Physics Report, UUIP-1232, 1990.

Abstract: A high resolution, monochromatized HeIIα, photoelectron spectrum of the 5s correlation satellites in Xe is presented. Approximately 70 new lines, previously not observed in photoelectron spectroscopy, were assigned using optical data. It is found that the dominating lines in the spectrum are associated with levels of high angular momentum.

Paper XI:

High resolution, monochromatized HeIIα excited, photoelectron spectra of N_2, CO and O_2.

M. Carlsson Göthe, P. Baltzer, L. Karlsson, B. Wannberg and S. Svensson.

Uppsala University Institute of Physics Report, UUIP-1233, 1990.

Abstract: The valence photoelectron spectra of N_2, CO and O_2 excited using monochromatized HeIIα radiation are presented. Due to the high resolution and high signal-to-background ratio obtained in these spectra extensive new vibrational structure has been observed. New assignments of some of the photoelectron bands have been made to fit with the new features observed in the spectra. Vibrational progressions have in may cases been followed almost all the way up to the dissociation limits. Morse potential curves have been calculated for the states with clear vibrational progressions. Some potential curves show anomalous behavior such as double potential wells.

Paper XII:

Inner Valence Satellite Structure in High Resolution X-ray Excited Photoelectron Spectra of N_2 and CO.

S. Svensson, M. Carlsson Göthe, L. Karlsson, A. Nilsson,
L. Mårtensson and U. Gelius.

Uppsala University Institute of Physics Report, UUIP-1200, 1989.
Submitted to Chem. Phys.

Abstract: The high resolution X-ray excited (hν = 1487 eV) valence photoelectron spectra of N_2 and CO are presented. The spectra show a rich line structure down to 65 eV binding energy due to electron correlation effects. Several new structures are observed and new assignments are made from comparisons with calculations, monochromatized HeII excited photoelectron spectra and resonance Auger electron spectra.

Paper XIII:

X-ray photoelectron, Auger electron and ion fragment spectra of O_2 and potential curves of O_2^{2+}.

M. Larsson, P. Baltzer, S. Svensson, B. Wannberg, N. Mårtensson,
A. Naves de Brito, N. Correia, M. P. Keane, M. Carlsson Göthe and L. Karlsson.

N. Phys. B **23**, 1175 (1990)

Abstract: The O_2^{2+} ion has been studied by means of electron-impact-induced and photon-induced Auger electron spectroscopy and oxygen ion fragment spectroscopy of O_2. The oxygen ion kinetic energy spectrum was recorded by inverting the relevant potentials of an electron spectrometer for the detection of positive particles. The $^4\Sigma^-$ and $^2\Sigma^-$ O1s initial core hole states have been studied using monochromatized X-ray photoelectron spectroscopy. Potential energy curves for a number of electronic states of the O_2^{2+} dication have been calculated with the complete active space SCF (CASSCF) and multireference contracted CI (MRCCI) methods with a 1-particle basis set of medium size ([8s, 6p, 2d]). An analysis of the O_2 Auger electron spectrum based on the computed potential curves of O_2^{2+} is presented. The autoionisation satellites are analyzed and it is found that these lines correspond to molecular singly ionized final states. One line at 510.7 eV, however, is associated with an atomic-like transition. Two shake-up Auger satellites are identified by a comparison with a recent O1s shake-up spectrum from O_2.

Paper XIV:

The NVV Auger electron spectrum of the HI molecule.

L. Karlsson, S. Svensson, P. Baltzer, M. Carlsson Göthe, M. P. Keane, A. Naves de Brito, N. Correia and B. Wannberg.

J. Phys. B 22, 3001 (1989).

Abstract: The electron-beam-excited NVV Auger electron spectrum of HI is presented together with a new recording of the X-ray excited photoelectron spectrum of the I4d core lines. It is shown that the initial I4d core hole state is vibrationally excited. The NVV Auger electron spectrum is dominated by transitions to the π^{-2} dicationic states of $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ symmetry. Vibrational structure is resolved in all Auger transitions and the equilibrium geometry of both the initial core-hole state and the final dicationic states have been determined. A splitting of the $^3\Sigma_1^-$ and $^3\Sigma_0^-$ states of the 220 meV is observed. The dissociation of the π^{-2} dicationic states in terms of Coulomb explosion is discusses and tentative potential curves are given.

Paper XV:

Vibrationally Resolved Study of the Fourth Photoelectron Band of Acetylene at 23.5 eV.

M. Carlsson Göthe, F.T. Chau, P.Baltzer, S. Svensson, B. Wannberg and L. Karlsson

Accepted for publication in Chem.Phys.Lett, 1990.

Abstract: The inner valence C $^2\Sigma^+_g$ electronic state of the acetylene cation has been studied by means of ultraviolet photoelectron spectroscopy using HeII excitation. Vibrational structure is resolved and is interpreted in terms of a vibrational progression in the totally symmetric $\nu_2(\sigma^+_g)$ mode. A Franck-Condon analysis has been carried out and force constants corresponding to the CH stretching, CC stretching and CH-CC stretching interaction have been determined. The CH and CC bond lengths have been deduced and the values are found to be 1.088 ± 0.005 Å and 1.439 ± 0.005 Å, respectively.

Paper XVI:

X-ray, UV and synchrotron radiation excited inner-valence photoelectron spectra of CH_4.

M. Carlsson Göthe, B. Wannberg, L. Karlsson, S. Svensson, P. Baltzer, F. T. Chau and M-Y Adam.

Accepted for publication in J. Chem. Phys 1990.

Abstract: The inner-valence electron states of the methane molecule have been studied by means of X-ray, synchrotron radiation and UV-photoelectron spectroscopy. Five correlation satellites have been identified and a detailed study has been carried out of the $2a_1^{-1}$ single hole state. For this state a Franck-Condon analysis has been performed, suggesting an equilibrium bond distance of 1.279 Å. The vibrational lines have a Lorentzian shape and the linewidth increases gradually with the vibrational quantum number. This probably indicates a reduction of the life-time of the vibrational states due to predissociation. A discussion of the potential curves related to the correlation satellites is included.

Paper XVII:

A high resolution HeI excited photoelectron spectrum of the H_2CO molecule.

M. Carlsson Göthe and L. Karlsson.

Uppsala University Institute of Physics Report, UUIP-1234, 1990.

Abstract: The HeI excited photoelectron spectrum of the H_2CO molecule has been recorded with high resolution. Detailed studies have been carried out of the vibrational structure observed in the four photoelectron bands. The vibrational energies and intensities have been determined using a curve fitting procedure. In the outermost band corresponding to the $X\ ^2B_2$ electronic state of H_2CO^+ a very extensive new vibrational structure is observed. It has been analyzed primarily in terms of different vibrational progressions in the ν_3 mode excited in various combinations with the ν_1 and ν_2 modes. These vibrational states are not reached in direct photoelectron transitions but must be due to the presence of an intermediate state in the photoionization process similarly to what has been found earlier for the CO molecule.

Paper XVIII:

Effects of relaxation and hyperconjugation on shake-up transitions in X-ray excited photoelectron spectra of some small carbonyl compounds.

M.P. Keane, S. Lunell, A.Naves de Brito, M. Carlsson Göthe, S. Svensson, B. Wannberg and L. Karlsson.

Uppsala University Institute of Physics Report, UUIP-1235, 1990.

Abstract: The C1s and O1s core shake-up and HeII excited valence photoelectron spectra of formaldehyde, acetaldehyde and acetone have been studied experimentally and by INDO-CI calculations. It is found that the presence of the π type orbitals on the CH_3 groups of acetaldehyde and acetone is responsible for the large differences found in the core shake-up spectra between these molecules and formaldehyde. Due to the redistribution of charge in the oxygen acetaldehyde and acetone core ionised systems, the energy ordering between the C=O π orbital and the CH_3 $^1b_1$ π type orbital is reversed, compared to the neutral molecules. The ionization from the $6a_1$ σ(C-O) orbital in acetone gives rise to a clearly observable vibrational progression whereas the corresponding orbital on formaldehyde is structureless. This indicates a substantial stabilization of the bonds due to the methyl substitution.

Paper XIX:

Observation of a double potential well in the C-state of the CO^+ molecule.

M. Carlsson-Göthe, B. Wannberg, L. Karlsson, S. Svensson and P. Baltzer

Uppsala University Institute of Physics Report, UUIP-1236, 1990.

Abstract: The C-state of CO^+ has been studied using UV photoelectron spectroscopy. The spectrum was excited by a monochromatized HeIIα ECR source. The vibrational progression in the C state has earlier been observed up to v=6 and an anomalous anharmonicity has been inferred. In the present spectrum the progression has been followed up to v=11 and the progression can be described as originating from two nearly harmonic potentials. A perturbation is thus found for the C state at an internuclear distance of about 1.4 Å. Moreover, the progression extends 0.2 eV above the dissociation limit and therefore a potential barrier must exist with a maximum around 2.3 Å.