(Invited paper to International Symposium on Future Applications of Inner Shell Ionization Phenomena, Atlanta, Georgia, April 22, 1972)

PRESENT AND FUTURE APPLICATIONS OF AUGER SPECTROSCOPY*

Thomas A. Carlson

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

ABSTRACT

Because of the high scattering cross section for low energy electrons in matter, studies on the Auger effect have been somewhat limited. However, in two situations, gases at low pressures and surfaces of solids, Auger electrons may be measured with ease. During the last few years increased attention has been paid to Auger spectroscopy as a means for studying other atomic and molecular properties. With gases Auger spectroscopy has been helpful in yielding information regarding initial excitation phenomena and the nature of doubly-charged molecules, as well as providing a method for gas analysis. With solids, Auger spectroscopy has become a powerful tool for surface analysis, especially when combined with other surface techniques such as low energy electron diffraction (LEED) and scanning electron microscopy. An outline of the present uses of Auger spectroscopy will be given together with some suggestions for the future.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

I. INTRODUCTION

When a vacancy is formed in one of the inner shells of an atom, it may be filled by either a radiative (X ray) or nonradiative process (Auger process). In most instances nature chooses the Auger process. Only when the transition energy exceeds roughly 10 keV does X-ray emission pre-dominant. Why then are X rays well known to even the man-in-the street, while the understanding of Auger processes have until recently been restricted to the specialist? The answer lies simply in the ease of measurement. X rays are a highly penetrating radiation, while Auger electrons have only a small mean-free-path in solids.

For the most part, the earlier studies of Auger processes were studies of a nuisance effect. One needed to know about these processes in order to correct his data. For example, the Auger effect has been of interest to the X-ray spectroscopist because of its profound alteration of the fluorescence yield, and because of the broadening of the natural widths of the X-ray lines caused by shortening of the lifetimes of the vacancy state. Nuclear spectroscopists have also needed to study the Auger process in order to better account for their data on electron capture and internal conversion, in which inner-shell vacancies are being promoted. If, for example, the probability for K capture for a given element is being monitored by the number of X rays observed, then the fluorescence yield must be ascertained. In the study of internally converted electrons, the beta spectroscopist also measures the discrete energy Auger electrons. Studies on the Auger effect did shed light on certain aspects of atomic physics such as the type of coupling (LS, jj or intermediate) that occurs throughout the periodic table,¹ but, in general, relatively little applied use was made of the phenomenon.

In the last few years this situation has drastically changed. Two media in which the collision cross section does not prevent the detection of even low energy Auger electrons are gases and surfaces of solids. The study of Auger electrons under these conditions has proven to be most profitable.

Studies of Auger electrons in gases have been useful in learning about the basic phenomena of ionization and about the nature of molecular ions, while in the study of surfaces Auger spectroscopy has been invaluable as an analytical tool. In this paper we shall discuss in detail the more recent applications of Auger spectroscopy in both gases and solids.

II. USE OF AUGER SPECTROSCOPY FOR GASES

The high resolution possible for measuring electrons ejected from a gas target and the simplifying conditions encountered when dealing with individual molecules or atoms, have made the study of the Auger spectra of gases a fruitful area for fundamental research. Details of the Auger process itself, the nature of the ground and excited states of the doubly charged ions, and the various phenomena associated with the initial excitation process are topics that will be discussed in this section. In addition we shall try to evaluate the potential for gas analysis using Auger spectroscopy.

A. Atoms

Mehlhorn² was first to demonstrate the advantages of studying the Auger spectra of gaseous atoms with high resolution. These studies gave fine details against which the concepts of the Auger process could be tested. Subsequently, additional data on rare gases were obtained at Uppsala³ and at Oak Ridge.⁴⁻⁶ Sodium vapor has also been studied by Mehlhorn.⁷

Auger spectra arising from filling the M and L shell as well as the K shell were taken, and even the low energy spectra due to Coster-Kronig transitions have been recorded.² An idea of the complexity of a well resolved Auger spectra is given by Fig. 1.

In addition to the normal Auger lines, whose energy spacings can accurately be checked by optical data, a wealth of other lines (satellite lines) are observed. For example, note the paper by Krause et al.⁴ on the K-LL Auger spectrum of neon. In this study some 90 lines were seen. Of these only five were the normal K-LL Auger lines expected from pure Russell-Saunders coupling. A sixth due to the forbidden $K-L_{III}L_{III}^3P$ transition was found with an intensity of 0.05% of the most intense line. The normal K-LL lines arise from transitions in which a single vacancy appears in the K shell for the initial state and two vacancies in the L shell occur for the final state; otherwise, the other electrons are in the same configuration as they would be for a neon atom. A satellite line occurs when the configuration is altered from that described either for the initial or final state. Figure 2 illustrates some of the types of processes that lead to satellite lines. These include monopole excitation and ionization (or electron shake up and shake off) that occur as the result of a sudden change in effective charge when the initial K vacancy is formed. Another important process is the excitation by electron impact of a K electron into an excited but neutral species that will then decay by auto-ionization. Extra ionization or excitation may also occur in the Auger process itself (sometimes called a double Auger process⁸). Each of these processes yield Auger satellite lines of characteristic energy. Although normal lines make up the bulk of the Auger spectrum, the contribution from satellite lines is by no means negligible.

B. Molecules

The first high resolution Auger spectra on molecules were taken by Stalherm et al.⁹ followed by a number of studies carried out by Siegbahn et al.^{3,10} and by Moddeman et al.¹¹ The Auger spectra of molecules are considerably more complex than the corresponding spectra for atoms. This is due in part to the larger number of molecular orbitals and in part to the added complexity of vibrational structure. Auger transitions between shells that are classed as inner shells (i.e., have principal quantum numbers that are smaller than that of the valence shell) will give binding energy shifts as a result of changes in chemical environment that are similar to those observed with photoionization.¹ More extensively studied and more interesting because of the unique information that is available are the K-LL Auger transitions, in which the L shell is the valence shell, which is to say Auger transitions for the first row elements including boron, carbon, nitrogen, oxygen and fluorine.

Moddeman et al.¹¹ have provided a generalized scheme for analyzing the various portions of the K-LL Auger spectra of molecules. It consists (1) of determining which portions are due to normal Auger processes and which are satellite peaks, (2) of dividing the normal Auger lines into categories as to whether they are derived from molecular orbitals whose electrons are weakly or strongly bound and (3) of identifying (with the help of theory or optical data) specific Auger peaks that are the result of transitions to specific molecular states.

One of the most important Auger peaks to identify is the highest energy normal Auger line, since from its energy one can ascertain the second ionization potential of a given molecule. In Table I are listed

$E_{II}(\text{min})$ for a number of molecules as obtained from Auger spectra, together with appearance potentials derived from mass spectroscopy. In one case, nitrogen, it was also possible from Auger data to estimate the energy necessary to form the triply-charged ion. In general, the agreement between values arrived at by Auger spectroscopy and those obtained by mass spectroscopy is good. Auger spectroscopy has one distinct advantage over mass spectroscopy in determining the minimum energy for forming molecular ions, since in mass spectroscopy the ion must remain intact approximately the 10^{-5} sec required to detect it, while meaningful results can be obtained from Auger spectra without the requirement that the doubly-charged ion remain stable. A core electron is nonbonding, and a vacancy in the core will generally not cause dissociation until after the Auger transition has taken place.

Besides the formal methods for analyzing molecular Auger spectra that have been discussed in the preceeding paragraphs, there are several other observations that can be of assistance. First, it is of value to compare the Auger spectra derived from different elements of the same molecule. The energy spacings for all spectra should correspond to that expected for the various states of the doubly-charged molecular ion that are the result of a K-LL Auger process. The total Auger energy depends strongly on the initial state or in other words which element has the initial K vacancy, but the energy spacings in the Auger spectra depend on the nature of the final states which are those of the molecular ion where the vacancies are all in the valence shell. The probability for reaching a given final state will depend on whether the valence shell molecular orbitals involved in the Auger transitions are strongly associated with the atom having the K hole. In Fig. 3 there is a comparison of the Auger spectrum corresponding to K vacancies in carbon and

oxygen of CO. The peaks are labeled identically when it is felt that they both represent the same final state. This information helps the assignment of the origin of various Auger peaks. For example, using population density analysis from molecular orbital calculations, one would expect that Auger processes filling a vacancy in the K shell of carbon would involve the $2p\sigma^b$ orbitals of CO more readily than would be the case if the K vacancy occurred in oxygen.

Another source of information for analyzing the Auger spectrum is from vibrational structure. Normally, such structure is not readily seen because of the complexity of the Auger spectrum and the stringent requirements for resolution. However, it has been observed^{3,11} quite clearly in the case of the carbon spectrum of CO.

Finally, Auger spectra can be analyzed by comparison of data for a homologous series of compounds. Spohr et al.¹⁰ have studied a series of brominated methanes, while Moddeman¹² has investigated fluorinated methane. Figure 4 shows the carbon KLL Auger spectra for methane, ethane and benzene. Spohr et al.¹⁰ noted that the sharpest lines are found in benzene, while the broadest are seen for methane. The authors explain this in terms of the lifetime for the doubly charged molecules. The dissociation energy for methane, ethane and benzene are estimated to be respectively -13, -8 and +1 eV, and the line broadening may also be expected to decrease in that order. The relative sharpness in the lines observed in the bromomethane compounds were also interpreted in terms of whether the Auger transitions involved with bonding orbitals lead to dissociative states.

C. Studies of Ionization Phenomena

In the preceding section we have emphasized the nature and identification of the various Auger lines. In obtaining this analysis we learned that many of the lines were satellite lines arising from some mode of initial excitation. These lines can thus be used as a means for following the nature of the excitation process.

We have already discussed in some detail the information gained on the types of excited states that are formed with K vacancies are created by electron impact. Glupe and Mehlhorn used the Auger spectra to determine the K shell ionization cross section of C, N, O, and Ne as a function of electron impact energy.¹³ Krause et al.⁴ showed that the satellite spectrum for neon representing initial shake-off and shake-up processes were essentially identical, whether produced by electron impact or photoionization. By comparing intensities of Auger satellite lines relative to the normal Auger lines, Carlson et al.⁵ studied the extent of electron shake-off as a function of electron impact energy. From these studies it has become clear that electron shake off as the result of inner shell ionization by electron impact can be treated by the sudden approximation, just as with photoionization. Rudd,¹⁴ using Auger spectroscopy, has followed the nature of ionization by protons, and finds in marked contrast to photoionization and electron impact much larger contributions for satellite lines than would be predicted by the sudden approximation. The present interest in the nature of multiple ionization by high energy heavy ions could also be assisted by Auger spectroscopy. Auger energies in highly charged ions will shift from that observed for an ion with a single inner shell vacancy. From both the Auger energies and relative intensities of Auger peaks one

can in principle analyze the extent of ionization and configuration for a given heavy ion. Both the target and projectile could be so studied. Such analyses have been made using X rays of the highly charged ions, and could be extended profitably to Auger spectra. In fact, shifts in Auger energies should be much more sensitive to the removal of outer shell electrons than the parallel shifts of X-ray energies.

D. Auger Spectroscopy for Use in Gas Analysis

Auger spectroscopy offers a number of advantages for gas analysis. In Fig. 5 are shown five oxygen K-LL Auger spectra from five different molecules. Though the center of the spectrum in each case is approximately 490 eV, indicating that we are dealing with the element oxygen, the details of the spectra are quite dissimilar, offering essentially a "finger print" for a given molecule. Thus, an Auger spectrum yields both an elemental analysis and molecular identification.

Auger spectra of gases can consist of highly resolved peaks. There is no line broadening from the excitation source as with photoelectron spectroscopy. The principal limitation to resolution comes from the natural width of the core electrons. In the case of carbon this has been shown to be less than 0.2 eV. The state of the doubly charged molecular ion following an Auger process should also be stable for at least 10^{-14} sec if the line broadening is not to be increased, but many molecules are able to meet this requirement. The intensity for producing Auger lines by electron impact can be made very high. It is easy to produce electron beams of 300 milliamps. I have found that only a small fraction of that current, 0.5 milliamps, would produce Auger lines with an intensity which was only limited by the saturation of our electron multiplier ($\sim 50,000$ c/sec)

when the pressure of the target gas was about 10 microns. The peak to background ratio is an important consideration if high sensitivity is being sought (parts per million). When X rays were used to produce inner shell vacancies, ratios as high as 30,000 to 1 were obtained. When electron impact was used, the best ratio was 500 to 1, and the importance of scattered electrons increased as one went to lower kinetic energies. However, with greater care for reducing secondary electrons, the peak to background ratios might be substantially improved.

There are limitations in the use of Auger spectroscopy as an analytical tool for gases. To analyze two or more molecules (say hydrocarbons) simultaneously by studying the Auger spectra of a common element (carbon) would be difficult, since the spectra would overlap. If the gases were present to about the same order of magnitude, and their spectral profiles well known, analysis would be possible, but not for trace amounts. A trace element might be studied, however, without interference, conceivably to a few parts per million. The use of Auger spectroscopy can be greatly enhanced by combining it with gas chromatography, as has been accomplished with mass spectroscopy.

Good resolution, high counting rates, unique identification of molecules, sensitive elemental identification, all make Auger spectroscopy a potentially powerful tool for gas analysis. As of yet, no systematic study of its analytical possibilities on gases has been made, but it would appear to be a worthwhile undertaking.

III. USE OF AUGER SPECTROSCOPY IN THE STUDY OF SURFACES

A. General Considerations

The first use of Auger spectra to aid in the analysis of surfaces was made by Lander¹⁵ in 1953, in which he studied various surfaces with low energy electrons (500-1000 eV) and measured the resultant Auger electrons that were emitted. The recent interest, however, was kindled by Scheibner and Tharp¹⁶ and by Weber and Peria¹⁷ in which Auger spectra measurements were coupled to a conventional low energy electron diffraction (LEED) system. In the few years since that time over a hundred papers have appeared using Auger spectroscopy as a tool for surface analysis.^{18,19}

Since the use of Auger spectroscopy for studying surfaces has come primarily from the work of surface scientists, more attention has been placed on surface cleanliness rather than high resolution. In contrast, photoelectron spectroscopy has been more concerned with better resolution. One field may be said to be clean but imprecise, the other, accurate but dirty. Actually, technology is potentially capable of achieving both goals, but at present these limitations still exist.

Whereas the LEED-Augur spectrometers may be open to criticism with regard to the most effective energy analysis, workers in this field have been most studious in their development of clean vacuum systems and in surface preparation. A pressure of 1×10^{-9} torr. is needed if one wishes to maintain a clean surface for 1 hour. Much of the LEED-Augur work is done in the 10^{-10} torr. range.

As an analytical tool Auger spectroscopy is quite successful for the lighter elements, particularly the first-row elements from $Z = 3$ to 10. The fluorescence yield is less than one percent, so that these

elements are difficult if not impossible to measure by use of their characteristic X rays. K vacancies are filled in nearly every case by an Auger process. In addition, the K-LL Auger spectra are relatively simple and quite distinctive as to the element involved. However, any element can be studied (except H and He) by Auger spectroscopy and researchers have now extended the method throughout the periodic table. Comprehensive tables based on atomic binding energies have been prepared²⁰ for all Auger transitions for energies between 10 and 3000 eV for elements up to $Z = 103$.

Auger spectroscopy for surface analysis has been used primarily for qualitative analysis. It is quite sensitive; 1 - 2% of a monolayer can generally be detected, and in some cases as little as 0.2 to 0.5% have been reported. The sensitivity in fact is limited by surface cleanliness rather than signal strength, since the cleanliness depends on time of exposure. It is also important to note that Auger spectra can be taken in milliseconds. In general, the cross section for inner shell ionization, and thus the sensitivity for detection, decreases with increasing binding energy. Therefore, the lower energy Auger processes that are still characteristic for a given element are the ones usually chosen for study, partly because of the greater cross section for producing these Auger processes and because such low energy Auger electrons will emanate from layers closer to the surface.

Quantitative analysis is in principal also possible. The relative intensities depend on a number of variables: inner shell ionization cross sections, Auger transitions rates, and inelastic scattering of the emitted Auger electrons. However, with careful calibration, one ought to be able to obtain quantitative analysis of a sample, assuming homogeneity, to an

accuracy of about 5%. If the sample is not homogeneous at the surface, auxiliary experiments will have to be made before a final interpretation is reached. Use of Auger spectroscopy in quantitative analysis is not a precise measurement, but it can still be of great help in studying the surface.

To emphasize the surface layers the angle between the electron beam and the surface plane of the target is made as small as possible (usually about 10^0). By changing the grazing angle of the electron beam, one can vary the relative contributions of the surface layers, and thus determine if there is any inhomogeneity of the chemical composition of the surface.

One of the chief advantages of Auger spectroscopy as an analytical tool for solids is that a small but intense beam of electrons can be used to survey the sample. A normal electron beam has a current from 10 to 100 μ amps with a focal spot of less than 1 mm diameter. Thus, individual small portions of the surface can be studied one at a time. Spatial resolution for Auger analysis has been achieved for areas smaller than 1 micron in diameter.²¹ (Cf. Fig. 6.) Auger spectroscopy has been wedded with other methods of surface analysis such as LEED (low energy electron diffraction) and electron microscopy, so as to yield simultaneously elemental analysis as information on structure is obtained.

B. Specific Applications

A complete literature survey of the use of Auger spectroscopy for surface analysis will not be attempted here (cf. Ref. 18, 19) but a sufficient number of examples will be cited to illustrate the scope of the field.

1. Surface impurities

Auger spectroscopy can detect foreign elements down to about 1% of a monomolecular layer. It has thus become the criterion for surface cleanliness. For example, in the study of methods for surface cleaning, it has been found that although electrical heating removes oxygen and carbon from nickel²² and steel,^{22,23} it also promotes diffusion of sulfur to the surface. Jenkins and Chung²⁴ found both carbon and sulfur diffused to the surface on heating of copper. Taylor²³ and Sickafus²⁵ demonstrated ion bombardment as a preferable method for cleaning the transition metals. Lambert et al.²⁶ studied the carbon overlay on Pt and also warned about the problem of cleaning Pt by heating.

2. Surface Coverage

Detailed studies can be made on the way in which surfaces are covered by means of Auger spectroscopy. For example, Weber and Johnson²⁷ measured the degree of depositing K ions into silicon and germanium from 0.1 to 1.0 of the first surface layer, finding a linear relationship. Palmberg²⁸ discovered the sticking coefficient of Xe on palladium (100) was independent of surface coverage up to 5.8×10^{14} atoms/cm² and then decreased suddenly to zero. A study of the absorption of oxygen on tungsten was made by Musket and Ferrante.²⁹ Pollard³⁰ investigated the growth of thorium on the tungsten (100) plane. The tungsten Auger peak was found not to be covered by thorium even after an equivalent of 25 monolayers were deposited. The conclusion was that the thorium nucleated so as to cover only 5% of the total surface.

Joyce and Neave³¹ studied the interaction of oxygen on silicon obtaining a sticking constant of 8×10^{-4} which was independent over 10^{-5} to

10^{-8} torr. The absorption was found to be initially rapid followed by a substantial change in rate as the monolayer neared completion.

Bonzel³² carried out careful studies on the absorption of oxygen onto a preabsorbed sulfur of Cu. He used this study to demonstrate the use of Auger spectroscopy in studying reaction rates. An example of his data is given in Fig. 7. He supplemented the Auger analysis with mass spectral analysis of the absorbed gases. From this study Bonzel concluded: (1) fast surface reactions between S and O can be measured by Auger spectroscopy; (2) the kinetics and partial dependence of surface reactions indicated a Langmuir-Hinshelwood mechanism and (3) as a consequence of high activation energies the reaction could be surface diffusion controlled.

3. Inhomogeneity between the bulk and surface

The inhomogeneity of a given material can be nicely studied by Auger spectroscopy. For example, rocks of geological interest may be studied in detail over their whole surface without breaking apart the sample. Such an analysis was carried out on lunar samples by Connell and Gupta.³³

Often the surface analysis of a supposedly homogeneous material is quite different than the bulk. Coad and Riviere³⁴ showed that carbon segregated to the surface of nickel foil and is present as Ni_3C below 673°K but turns to graphite about $673^\circ - 873^\circ\text{K}$. This kind of segregation often occurs with sulfur impurities in metals as the result of heat treatment and has been so measured by Auger spectroscopy^{23,35} as was mentioned earlier. It was further found that fracturing of steel occurs along grain boundaries containing antimony, these boundaries being only a couple of atomic layers thick. See, for example, the work of Marcus and

Palmberg³⁶ in Fig. 8, which shows the presence of antimony in embrittled steel.

Auger spectroscopy could also be employed for the study of slow diffusion, particularly where knowledge of a very sharp profile, the order of a monolayer, is required.

4. Radiation Damage

One of the problems that faces the use of a high intensity, sharply focused electron beam is radiation damage. This problem can be turned to advantage by the study of surfaces as the result of electron bombardment. For example, Palmberg and Rhodin³⁷ and later Tokutaka et al.³⁸ investigated the surface dissociation of KCl under electron irradiation. The desorbed neutral particles of K, Cl, and Cl₂ were measured by mass spectroscopy, while the surface concentration was analyzed by Auger spectroscopy. For temperatures above 60°C surface stoichiometry was maintained, but below that value, there was a net loss of Cl. Desorption of absorbed gases such as oxygen on tungsten³⁹ and CO on silicon⁴⁰ have been studied by Auger spectroscopy. In the latter case it was determined that the radiation damage occurred in a two step process: (1) CO is dissociated and (2) the carbon diffuses over the surface while oxygen remains fixed. This was ascertained by monitoring different portions of the surface by Auger spectroscopy, but maintaining constant irradiation only at one point.

5. Molecular Identification

As has been pointed out previously in this paper, Auger spectroscopy of solids is primarily used for elemental identification. But from studies on gases (Cf. Fig. 5) it is obvious that Auger spectra are

also characteristic of the chemical environment. As higher resolution electron spectroscopy is used in surface studies, greater application of chemical analysis will be made. Grant and Haas⁴¹ have used Auger spectroscopy to distinguish between the carbon in graphite and in silicon carbide. These authors⁴² have also noted a chemical shift in the ruthenium Auger spectra as the result of the presence of carbon on the surface of ruthenium. Joyce and Neave³¹ found that the Auger spectrum for silicon oxidized on the surface at high temperatures was considerably different from that found with silicon which had a high coverage of absorbed oxygen, which indicated different chemical environments for the silicon. Chemical identification of mixtures of Be and BeO and of Al and Al₂O₃ have also been made through their distinctive Auger spectra.^{43,44,45} For example, see Fig. 9.

6. Combination of Auger Spectroscopy with Other Surface Techniques

Auger spectroscopy is a particularly powerful tool when it can be combined with other techniques for studying the surface. Auger spectroscopy in fact received its initial impetus as the result of combining it with LEED. Low energy electron diffraction gives information on the structure of the surface of a crystal. (It is restricted to measurements of a single crystal.) LEED is generally insensitive to the detection of impurities and gives information on structure, but not the elemental composition of the surface. Auger spectroscopy does this admirably and offers an ideal complement to LEED. For example, on cleaning Pt a 1x5 pattern occurred in the LEED measurements, which was explained⁴⁶ with the help of Auger spectroscopy by the raising of oxygen impurities below the surface to close to the surface such as to cause an undulating surface and thus the 1x5 pattern.

As with LEED, scanning electron microscopy utilizes an electron beam so that the opportunity for Auger spectroscopy is also provided simultaneously. As one maps the topographical features of a material by electron microscopy, one can in principal also carry out a chemical analysis by Auger spectroscopy. MacDonald and Waldrop²¹ have given a particularly nice demonstration of the value of combining scanning electron microscopy with Auger spectroscopy, and have discussed its potentialities. (Cf. Fig. 6.)

Auger spectroscopy can be used successfully with a variety of other surface techniques: X-ray photoelectron spectroscopy in which both Auger and photoelectrons are produced in the same spectrum, high energy electron spectroscopy for finding information regarding the structure of a material in the vicinity of the surface, and mass spectroscopy for analyzing desorbed gases and other particles ejected from the surface. Such an interweaving of these and other physical techniques has given rise to a substantial advancement in the field of surface science.

CONCLUSION

After many years Auger spectroscopy is coming into its own as a tool for studying other phenomena. Studies done on gases at low pressure and on surfaces of solids have been particularly successful since under these conditions low energy Auger electrons can be easily detected. Application has been made to basic problems in atomic and molecular physics such as in the study of doubly charged molecular ions and the nature of excitation processes. Likewise, Auger spectroscopy can be put to the service of more applied problems such as in the study of surface phenomena and for chemical analysis of both solids and gases. This paper

gives only a small inkling of the present use of Auger spectroscopy, and of the new applications which we may expect to occur in the future.

TABLE I

Minimum energy (eV) required for producing doubly and triply
charged molecular ions

Ion	Auger spectra ^a	Mass spec. ^b
N_2^{2+}	42.9	42.7
N_2^{3+}	84	
O_2^{2+}	37.4	36.5
CO^{2+}	40.2	41.8
NO^{2+}	35.4	39.8
H_2O^{2+}	39.2	
CO_2^{2+}	37.6	36.4
CH_4^{2+}	35.0	
CH_3F^{2+}	35.0	
CHF_3^{2+}	36.9	
CF_4^{2+}	40.4	

^aCf. Moddeman et al. ref. 11 and 12.

^bJ. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron,
K. Draxl and F. H. Field, Nat'l Std. Ref. Data Ser., Nat'l Bur. Std.
26, (1969).

REFERENCES

1. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, Y. Hedman, G. Johansson, T. Bergmark, S-E. Karlsson, I. Lindgren and B. Lindberg, "Electron Spectroscopy for Chemical Analysis," *Nova Acta Regiae Soc. Sci. Upsaliensis Ser. IV*, 20 (1967).
2. W. Mehlhorn, *Z. für Physik* 187, 21 (1965); W. Mehlhorn, *Phys. Letters* 15, 46 (1965); H. Körber and W. Mehlhorn, *Z. für Physik* 191, 217 (1966); W. Mehlhorn, *Z. für Physik* 208, 1 (1968); W. Mehlhorn, D. Stalherm and H. Verbeek, *Z. Naturforschung* 23, 287 (1968).
3. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne and Y. Baer, "ESCA: Applied to Free Molecules" (North-Holland, Amsterdam, 1969).
4. M. O. Krause, F. A. Stevie, L. J. Lewis, T. A. Carlson and W. E. Moddeman, *Phys. Lett.* 31A, 81 (1970).
5. T. A. Carlson, W. E. Moddeman, and M. O. Krause, *Phys. Rev. A* 1, 1406 (1970).
6. M. O. Krause, T. A. Carlson and W. E. Moddeman, *Jour. de Physique* 32, C-4, 139 (1971).
7. W. Mehlhorn (private communication).
8. T. A. Carlson and M. O. Krause, *Phys. Rev. Letters* 14, 390 (1965); 17, 1079 (1966).
9. D. Stalherm, B. Cleff, H. Hillig and W. Mehlhorn, *Z. Naturforsch.* 24, 1728 (1969).
10. R. Spohr, T. Bergmark, N. Magnusson, L. O. Werme, C. Nordling and K. Siegbahn, *Physica Scripta* 2, 31 (1970).
11. W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, *J. Chem. Phys.* 55, 2317 (1971).

12. W. E. Moddeman, Oak Ridge National Laboratory report No. ORNL-TM-3013 (1970) (thesis, University of Tennessee).
13. G. Glupe and W. Mehlhorn, Physics Letters 25A, 274 (1967).
14. A. K. Edwards and M. E. Rudd, Phys. Rev. 170, 140 (1968); D. J. Volz and M. E. Rudd, Phys. Rev. A2, 1395 (1970).
15. J. J. Lander, Phys. Rev. 91, 1382 (1953).
16. E. J. Scheibner and L. N. Tharp, Surface Sci. 8, 247 (1967); L.N.Tharp and E. J. Scheibner, J. Appl. Phys. 38, 3320 (1967).
17. R. E. Weber and W. T. Peria, J. Appl. Phys. 38, 4355 (1967).
18. For a bibliography, see T. W. Haas, G. J. Dooley, III, J. T. Grant, A. G. Jackson and M. P. Hooker, "Progress in Surface Science, vol. I, part 2," editor S. G. Davison (Pergamon Press, Oxford, 1971).
19. For two excellent reviews on the subject see: A. Pentenero, Catalysis Reviews 5, 199 (1971); C. C. Chang, Surface Sci. 25, 53 (1971).
20. R. N. Yasko and R. D. Whitmoyer, J. Vacuum Sci. and Tech. 8, 733 (1971); W. A. Coghlan and R. E. Clausing, ORNL-TM-3576 (1971).
21. N. C. MacDonald and J. R. Waldrop, Appl. Phys. Letters 19, 315 (1971).
22. L. A. Harris, J. Appl. Phys. 39, 1428 (1968).
23. N. J. Taylor, J. Vacuum Sci. and Tech. 6, 241 (1969).
24. L. H. Jenkins and M. F. Chung, Surface Sci. 24, 125 (1971).
25. E. N. Sickafus, Surface Sci. 19, 181 (1970).
26. R. M. Lambert, W. H. Weinberg, C. M. Comrie, J. W. Linnett, Surface Sci. 27, 653 (1971).
27. R. E. Weber and A. L. Johnson, J. Appl. Phys. 40, 314 (1969).
28. P. W. Palmberg, CNRS Colloquium on the Structure and Properties of Solid Surfaces, Paris, 1969, p. 31.

29. R. G. Musket and J. Ferrante, *J. Vacuum Sci. Tech.* 7, 14 (1970).
30. J. M. Pollard, *Surface Sci.* 20, 269 (1970).
31. B. A. Joyce and J. H. Neave, *Surface Sci.* 27, 499 (1971).
32. H. P. Bonzel, *Surface Sci.* 27, 387 (1971).
33. G. C. Connell, Y. P. Gupta, P. Kraatz, and R. F. Schneidmiller,
Proc. of the Second Lunar Sci. Conf., *Geochim. et Cosmochim. Acta*
Supp. 2, vol. 3 (M.I.T. Press, Cambridge, Mass., 1971) p. 2083.
34. J. P. Coad and J. C. Riviere, *Surface Sci.* 25, 609 (1971).
35. L. A. Harris, *J. Appl. Phys.* 39, 1428 (1968).
36. H. L. Marcus and P. W. Palmberg, *Transaction of the Metallurgical*
Society of AIME, 245, 1664 (1969).
37. P. W. Palmberg and T. N. Rhodin, *J. Phys. Chem. Solids* 29, 1917 (1968).
38. M. Tokutaka, M. Prulton, I. G. Higginbotham and T. E. Gallon, *Surface*
Sci. 21, 233 (1970).
39. R. G. Musket, *Surface Sci.* 21, 440 (1970).
40. J. P. Coad, A. E. Bishop and J. C. Riviere, *Surface Sci.* 21, 253 (1970).
41. J. T. Grant and T. W. Haas, *Phys. Lett.* 33A, 386 (1970).
42. J. T. Grant and T. W. Haas, *Surface Sci.* 21, 76 (1970).
43. D. T. Qunito and W. D. Robertson, *Surface Sci.* 27, 645 (1971).
44. R. J. Fortner and R. G. Musket, *Surface Sci.* 28, 339 (1971).
45. M. Suleman and E. B. Pattinson, *J. Phys. F: Metal Phys.* 1, L.21 (1971).
46. J. T. Grant and T. W. Haas, *Surface Sci.* 18, 457 (1969).

FIGURE CAPTIONS

- Fig. 1. Neon K-Auger spectrum excited by 4.5 keV electrons. Energy resolution 0.06% FWHM. A lines are normal Auger lines; the remaining peaks are due to satellite processes. (Cf. Krause et al. ref. 6).
- Fig. 2. Designation and description of K-LL Auger processes. K stands for a vacancy in the K shell, W for a vacancy in a weakly bound orbital (usually derived from a 2p orbital), S indicates a vacancy in a strongly bound orbital (usually derived from a 2s orbital, while e indicates an electron excited into an unoccupied orbital. In the level diagram 0 indicates a hole; X an electron. (Cf. Moddeman et al. ref. 11).
- Fig. 3. Comparison of K-LL Auger spectra for C and O of CO. The spectra are centered so that the energy difference in the scales equals the difference in the K binding energies. Similar numbers are used when the peaks represent the same final state of the molecular ion. The inserts in the carbon spectra show vibrational structure. (Cf. Moddeman et al. ref. 11).
- Fig. 4. Comparison of K-LL Auger spectra for methane, ethane and benzene. As one goes from methane to benzene the dissociation energies become less, and the sharpness of the Auger lines increase. (Cf. Spohr et al. ref. 10).
- Fig. 5. K-LL Auger spectra resulting from ionization in the K shell of O for different molecules. (Cf. Moddeman et al. ref. 11).

Fig. 6. Study of iron-copper composite sample using scanning electron microscope. a) secondary electron micrograph, b) Auger image of iron (oval), c) Auger image of copper (background). (Cf. MacDonald and Waldrop, ref. 21).

Fig. 7. Concentration of absorbed surfaces as a function of reaction time for constant temperature and partial pressure of oxygen. I_{32} is a direct measure of the partial pressure of oxygen. (Cf. Bonzel, ref. 32).

Fig. 8. Auger spectra of embrittle and de-embrittled steel. Note the presence of Sb in the embrittled steel. (Cf. Marcus and Palmberg, ref. 36).

Fig. 9. Auger spectra during progressive cleaning of pure Al sample. Curve (a) is essentially due to Al_2O_3 , (b) is due to $Al+Al_2O_3$, (c) is due to "clean" Al. (Cf. Quinto and Robertson, ref. 43).

FIGURE 1

DESIGNATION OF AUGER LINES

DESIGNATION	DESCRIPTION	INITIAL CONFIGURATION	FINAL CONFIGURATION	CHARGE OF ION
K-WW	NORMAL			2
K-WS	NORMAL			2
K-SS	NORMAL			2
Ke-W	EXCITATION OF K SHELL ELECTRON INTO DISCRETE STATE, FOLLOWED BY DECAY INVOLVING EXCITED ELECTRON			1
Ke-WWe	EXCITATION OF K SHELL ELECTRON INTO DISCRETE STATE, <u>NOT</u> INVOLVING EXCITED ELECTRON			1
KWe-WW	MONOPOLE EXCITATION FOLLOWED BY DECAY INVOLVING EXCITED ELECTRON			2
KWe-WWWe	MONOPOLE EXCITATION FOLLOWED BY DECAY <u>NOT</u> INVOLVING EXCITED ELECTRON			2
KW-WWW	MONOPOLE IONIZATION			3
K-W'WW	DOUBLE AUGER IONIZATION			3

FIGURE 2

FIGURE 3

ESCA

FIGURE 4

a

b

c

FIGURE 6

—Auger spectra of fracture surface of AISI 3340 steel;
(a) embrittled; (b) unembrittled.

FIGURE 8

Auger spectra during progressive cleaning of pure Al sample. Curve (a) is essentially due to Al_2O_3 , (b) is due to $\text{Al} + \text{Al}_2\text{O}_3$, (c) is due to "clean" Al.

FIGURE 9