X-rays from Heavy Ions: New Molecular Phenomena

Collisions of heavy ions with atoms have been studied for many years, but only recently the availability of high-resolution techniques to measure the x-rays thereby induced has led to a renaissance in experimental activity. Neither the copious numbers nor the complex patterns of x-rays produced by heavy ions are understood very well, but one theoretical model that has been proposed will explain most of the phenomena, at least qualitatively, and there is a hint that some of the effects observed may be interpreted in terms of very heavy elements. Although most efforts to date have been directed toward understanding the fundamental processes of the collisions, some scientists have already begun to develop related techniques for studying the chemical compositions of air particulates, the locations of impurities in semiconductors, and the detailed properties of surfaces.

The x-rays that have recently been the center of attention occur spontaneously after a heavy particle displaces an electron from an atom, causing a vacancy. As another electron in the atom shifts its orbital and its energy to fill the vacancy, radiation of x-ray wavelengths is often emitted. Thus, the x-ray properties tell an investigator something about the state of the atom. The outer electrons of an atom determine to a large extent its chemical properties, and in solids the properties of these loosely bound "Fermi" electrons can be measured in many ways. Inner shell electrons, on the other hand, are so tightly bound to the nucleus that their effects on chemical properties are minimal, and much less is known about them. While the "Fermiology" of matter is extensively explained in textbooks, the understanding of non-Fermi electrons is another matter entirely. The surprising and intriguing effect that physicists have observed in examining the x-rays that follow collisions of heavy ions with atoms is that vacancies can be created in inner shell orbitals almost every time an ion comes close to an atom.

Vacancies in the inner shells of atoms can also be produced by protons and alpha particles, which, unlike heavy ions, do not have electron clouds about them. (The classical method, bombardment with electrons, will produce inner shell vacancies too.) However, the probability that heavy ions will produce such vacancies may be as much as 1 million times greater than the probability for lighter projectiles, such as protons. At the same time, heavy ions are far more likely to produce multiple vacancies in a single collision (Fig. 1). The spectrum of x-ray wavelengths resulting from bombardment of titanium with protons indicates that only one or two vacancies are usually produced, but as many as six vacancies in inner shells, indicated by six peaks in the lowest part of the figure, may occur when titanium is bombarded with oxygen. (In this case, the projectile was an oxygen ion stripped of five of the eight electrons of the oxygen atom.) For bombardment by alphas the number of vacancies created is between the numbers for protons and oxygen ions. The leftmost peak has traditionally been called the "diagram line," which is most intensely excited by electron bombardment. The other lines, called satellites, are shifted somewhat from the wavelength of the diagram line because the nuclear charge is less effectively screened by electrons when more vacancies are created.

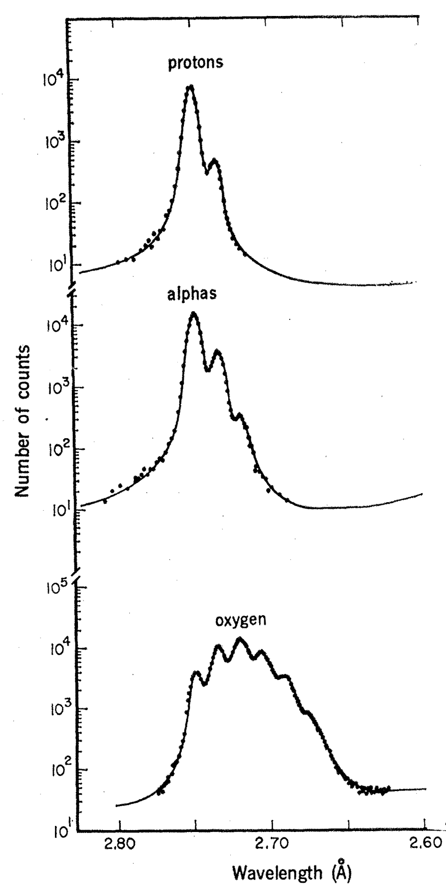

Fig. 1. X-ray spectra obtained when titanium is bombarded with various ions. The multiple peaks in the spectrum for oxygen ions indicate more electron vacancies were created.

The high-resolution spectra in the figure were obtained with a crystal spectrometer to measure the energies of x-rays induced by ions from a tandem Van de Graaff accelerator. For the case of oxygen, the ion energy was 30 million electron volts (Mev). The experiments were performed by Patrick Richard and colleagues at the University of Texas, Austin. Similar studies have been performed by Al Knudson, David Nagel, and associates at the Naval Research Laboratory (NRL) in Washington, D.C., using a variety of heavy ions, such as 15-Mev neon. Many such experiments can be performed with heavy ion beams from the powerful accelerators normally devoted to nuclear research because such heavy ions, even though their energies are high compared to those typical of atomic phenomena, have velocities comparable with the velocities of atomic electrons. Other experiments involving heavy ion–atom collisions can be performed with much less energetic ions [at energies of a few hundred thousand electron volts (kev)], which can be produced without large accelerators, and in fact several aspects of the anomalous behavior of heavy ions are most exaggerated at lower energies.

How does the impact of a heavy ion carrying a cloud of electrons differ from the impact of a bare proton? The creation of inner shell vacancies by protons or alphas appears to be a rather simple process, in that the likelihood of x-ray production changes relatively slowly with the atomic number of the target or the energy of the ion. Proton-induced x-rays can be successfully explained by a rather straightforward model, namely, ejection of the inner shell electron by the Coulomb interaction with the charge of the proton.

With heavy ion bombardment, however, the likelihood of x-ray production rises and falls dramatically with increases in the atomic number of the target material, and sharp thresholds appear which the ion energy must exceed before significant x-ray production takes place. R. J. Fortner and colleagues at the Lawrence Livermore Laboratory in Livermore, California, found that when copper ions with 160-kev energy struck targets with atomic numbers between 10 and 90 a wavelike effect occurred. Distinct peaks in the x-ray production probabilities occurred whenever the binding energy of electrons in inner shells of the target matched the binding energy of electrons in copper. In different studies, James A. Cairns at the Atomic Energy Research Establishment (AERE), Harwell, England, has exploited the threshold effect to determine the concentrations of implanted impurities like boron in the surface of a silicon crystal. The selectivity of this technique can be enhanced by measuring only very low energy x-rays.

Both the threshold effect and the wavelike effect, as well as the large likelihood for producing x-rays with heavy ions, can be explained by a model in which electron orbitals are distorted as an ion and an atom approach each other. In the collision of two identical atoms, this effect can be understood as the result of the Pauli principle. The idea of the molecular orbital model, as elaborated in 1965 by William Lichten of Yale University, New Haven, Connecticut, and Ugo Fano of the University of Chicago, Chicago, Illinois, is that a quasimolecule is formed very briefly as the ion and atom approach and recede from each other. As the electronic systems of the two atoms touch, energy levels of filled and unfilled molecular orbitals may cross with the result that electrons can leave in orbitals different from those in which they entered, thus creating vacancies. Subsequent filling of the vacancies may, of course, produce x-rays.

The threshold effect can be explained by the molecular orbital model because the threshold occurs when the ion is just energetic enough to reach the distance where level crossing occurs. Although most applications of the molecular orbital theory have been qualitative, recently John Briggs at AERE and Joseph Macek at the University of Nebraska, Lincoln, have performed quantitative calculations for the production of inner shell x-rays for a specific case, namely, neon-neon collisions.

In addition to evidence, such as that in Fig. 1, for copious production of inner shell vacancies, a more exotic phenomenon has recently been reported that is nevertheless understandable within the framework of the molecular orbital model. As two atoms move closer together, the molecular orbitals are eventually transformed into the orbitals of the atom that has an atomic number equal to the sum of the atomic numbers of the two colliding partners. Thus, Frans Saris at the Chalk River Nuclear Laboratories, Chalk River, Ontario, Roman Laubert at New York University, and their colleagues have reported argon ion–argon atom collisions in which they observed an x-ray transition which is not characteristic of either argon system but rather appears to be characteristic of a particular orbital in the argon-argon quasimolecule that is very similar to an orbital of the combined atom of krypton.

X-rays of Superheavy Elements

Although some investigators have questioned the explanation of the observed effect, the experiment has led more than a few physicists to speculate that by forcing two of the heavier stable elements to collide one might be able to see the x-ray spectrum of a superheavy element even before any superheavy elements are produced! At a conference on Inner Shell Ionization Phenomena held at the Georgia Institute of Technology, Atlanta, between 17 and 22 April 1972, P. H. Mokler from the Kernforschungs Anlage, Jülich, Germany, reported preliminary evidence for x-rays that could be characteristic of superheavy elements.

Another study related to the quasimolecular idea is the examination of the charge states of heavy ions as they pass through matter. Quite a bit is known about the most likely charge of a heavy ion after it comes out of a target, but the details of the electron swapping that determines the charge of the emerging ion are not so well known. Sheldon Datz and colleagues at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, have studied x-rays of iodine atoms passing through gas and solid targets. Often, x-rays are produced in a two-collision process. In the first collision, a vacancy in the ion's inner shell is created, and in the second collision this vacancy is transferred to the target. By comparing the results for solid and gas targets, for which the differences in elapsed time between collisions can be quite large, the charge of the ion during the second collision can be determined.

Although the major research efforts are focused on heavier ions, most applications use protons. Many physicists propose application of the techniques of ion-induced x-rays to the study of surfaces, particularly the concentrations of impurities in the first few monolayers. Paul Needham at the College Park, Maryland, station of the Bureau of Mines, Department of the Interior, has used proton-induced x-rays to determine concentrations of impurities at the surfaces of various iron alloys for several years. Techniques of ion-induced x-rays are often used in conjunction with other techniques. W. F. Van der Weg at the Philips Research Laboratory, Amsterdam, the Netherlands, and colleagues at the Foundation for Fundamental Research on Matter (FOM), Amsterdam, have recently compared proton-induced x-ray methods with proton backscattering. Needham has compared the measurements of surfaces by proton-induced x-rays and "auger" electron techniques. (In the process of deexcitation of an atom, either electrons or x-rays may be emitted.) Although few experiments with ions heavier than protons have yet been done, proponents of heavier ions cite as advantages compared to protons lower background radiation and shallower penetration into the solid. Less enthusiastic investigators, however, point out that it is not known how much heavier ions might damage a surface.

Another application of ion-induced x-ray techniques is in the chemical analysis of trace elements. Several laboratories are using proton or alpha beams to analyze such substances as air particulates, water samples, and the heavy element content of tissues of patients treated by hemodialysis.

The number of scientists interested in both the applications of heavy ion phenomena and the physics of the phenomena appears to be growing, and the results of recent research appear to have verified, at least at low energies, the validity of the molecular orbital model for ion-atom collisions. However, several clearly established phenomena are still open to detailed explanation.—WILLIAM D. METZ