

Seeing with a New Light: Synchrotron Radiation

R. E. Watson and M. L. Perlman

Synchrotron light—the light emitted by relativistic electrons when their path is bent by a magnetic field—has certain special properties which make it highly interesting to the researcher or applied technologist working with photons at ultraviolet or x-ray wavelengths. To generate this radiation electron energies of several hundred million to a few billion volts are required, and investigators, in increasing numbers, have been visiting electron accelerator facilities devoted primarily to high-energy physics in order to carry out experiments in the photon beams. The results obtained in the last

is considerable justification for this provision, in our view at least, and our purpose in this article is to describe the properties of the radiation, present a number of studies done with it, and suggest some of the possibilities for the future.

Characteristics of Synchrotron Radiation

Electrons having energies large compared with their rest energy and therefore velocities very near that of light, when constrained as by a magnetic field

entially, takes the form of a thin flat sheet in the orbital plane. Out of the plane, the intensity falls off rapidly; more than half the power is within a vertical angle $\sim 1/\gamma$ radians, where γ is the ratio of total electron energy to the rest energy. For a 1 billion electron volt (1 GeV) electron, $1/\gamma = 1/1957$. Radiation in the orbit plane has its electric vector lying in that plane; in other words, the light is highly polarized. In Fig. 1 synchrotron radiation spectra are shown for several values of electron energy and magnetic field. With logarithmic coordinate scales for photon intensity and wavelength, the curves have a universal form characterized by a wavelength (in angstroms)

$$\lambda_c = 5.59 R/E^3 = 186.4/B E^2$$

where R , E , and B are the orbit radius, electron energy, and magnetic field in meters, GeV, and kilogauss, respectively. At wavelengths shorter than λ_c the photon intensity decreases rapidly, but at longer wavelengths it falls only gradually. The spectra are continuous and smooth without the peaks and structure shown by other sources, and wavelengths otherwise unobtainable or available at only feeble intensity are readily had by monochromatization. Intensities and power are high; 1 ampere of 2.5-GeV electrons orbiting in a 10-kilogauss magnetic field emits more than 400 kilowatts as photon power.

Other characteristics of synchrotron radiation beams derive from the functioning of the equipment needed to maintain the electrons in circulation. Both electron synchrotrons and storage rings have been used to provide photon beams. Synchrotrons are circular accelerators intended primarily for the production of beams of energetic electrons. They operate cyclically, increasing the electron energy from some low initial value to a maximum, at which point the electron beam is ejected and utilized and the process is reinitiated. Cycle rates are of the order of several per second. In storage rings, on the other hand, the injected electrons are brought up to a final energy and maintained in orbit at this energy, often for hours. Synchrotrons and especially storage rings require orbit chambers at high vacuum, 10^{-7} to 10^{-10}

Summary. The special properties of synchrotron light are leading to a rapid increase in its utilization for both research and technology. At wavelengths in the ultraviolet region of the broad spectrum in these beams a number of atomic, molecular, and solid-state spectroscopies are being pursued; soft x-rays are being used for spectroscopy, lithography, microscopy, and topography; at still shorter wavelengths, advantage is taken of scattering properties to probe the structure of matter. Characteristics of synchrotron radiation and of the sources which produce it are described, and some typical investigations and applications are presented to suggest the versatility of these sources.

several years make it clear that research with synchrotron radiation is having an impact not only on the physical sciences but on the life sciences as well. Both in the United States and abroad support for this work has been increasing, and in the presidential budget for fiscal year 1978 there is provision for construction of the first U.S. facilities designed specifically as generators of synchrotron light. There

to a curved path, emit radiation whose directional pattern and frequencies are very different from those associated with classical accelerating charges. The angular distribution is transformed from the ordinary dipole pattern to one that is peaked sharply forward, and the spectrum is not the single oscillator frequency but, because of the forward focusing and Doppler effect, consists mainly of very high overtones.

Thus, for a horizontal circular orbit, the radiation, emitted everywhere tan-

R. E. Watson is a physicist and M. L. Perlman is a senior chemist at Brookhaven National Laboratory, Upton, Long Island, New York 11973.

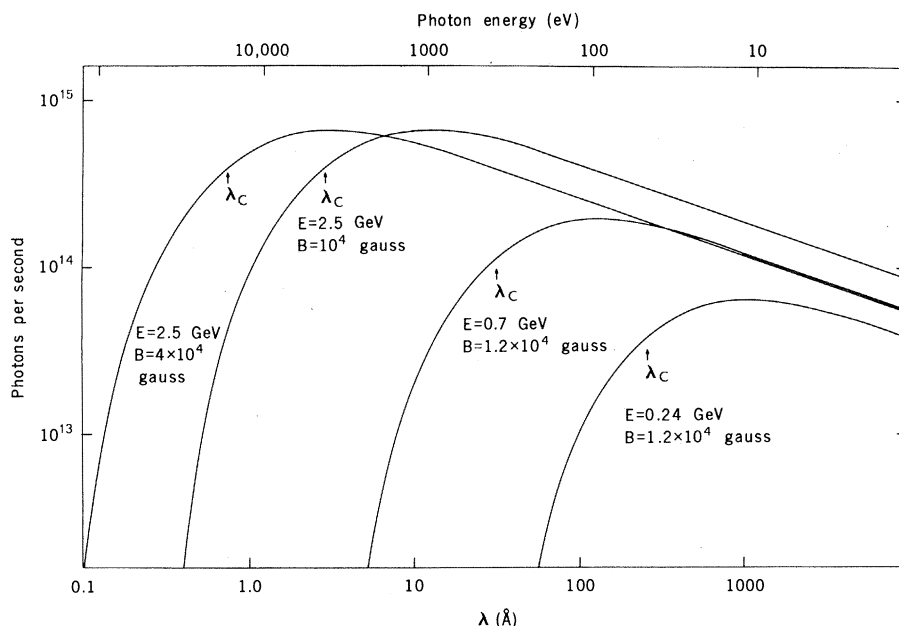


Fig. 1. Synchrotron radiation spectra for several typical electron energies and bending magnet fields. Intensities are given for a 1 percent bandwidth, for an electron current of 100 milliamperes, and in a 10-milliradian horizontal slice of the radiation.

torr. In storage rings the currents, and consequently the photon beam intensities, decay slowly and generally smoothly because of losses due mainly to electron-gas molecule and electron-electron scattering effects. Energy lost as radiation is restored to the electrons in passage through a radio-frequency (RF) cavity. The circulating current, perforce phased with respect to this radio frequency, is thus bunched, each of the one or more bunches being typically 5 to 30 centimeters in azimuthal length. The photon beam emitted from any point of the orbit is consequently in pulses of duration less than $\sim 10^{-9}$ second, and the circumference of a ring is such that the repetition rate is a few per microsecond if only one bunch is circulating.

Storage rings have many advantages over synchrotrons for photon beam production: there are no variations in intensity and in spectral characteristics caused by cycle-to-cycle fluctuations; radiation backgrounds in experimental areas are lower around rings with stored current than around cycling synchrotrons because electron loss rates are comparatively high during injection and early acceleration; and finally, the position stability of the electron orbit in a steady storage condition is generally better, a characteristic important for optical performance. Storage rings can be designed around the qualities desired in an optical instrument. Electron beam cross sections at some orbit locations can be made very small, of the order of a few hundredths of a millimeter high by a few tenths wide; such dimensions, in combi-

nation with the small vertical photon beam divergence already mentioned, result in extremely high source brightness—a quantity important for any experiment which requires focusing of the light.

A typical ring, designed for 700-MeV electrons and for the production of ultraviolet and soft x-rays, is sketched in Fig. 2. Electrons circulate counterclockwise in the vacuum chamber and photon beams are transported in the beam pipes seen tangent to the curved bending magnets. Adjacent to these simple dipole magnets are quadrupole and sextupole magnets, electron lenses which control some of the orbital properties. The RF cavity, which furnishes the energy lost by radiation, is in one of the four straight sections, and the inflector which directs the electrons when they are injected is in another. "Wigglers," special optical sources to be discussed below, are shown occupying the two remaining straight sections. This machine is ~ 7 meters in radius; a 2- to $2\frac{1}{2}$ -GeV machine, suitable for x-ray production, would be approximately 25 m in radius.

Modification of the synchrotron radiation spectrum. The synchrotron radiation spectra plotted in Fig. 1 are those observed at orbit locations where the radius of curvature R is produced by bending magnets of machines such as that diagrammed schematically in Fig. 2. Quite different spectra result from the orbits produced by certain periodic magnet structures (*1*). In one such structure, the vertical magnetic field alternates in direction, up and down, along the length

traversed by the electrons; in another structure, the field direction, normal to the orbit direction, rotates as one moves along the orbit direction to describe a helix. If the field in either structure has a periodicity length P , the field acting on the electron in its frame of reference has a periodicity P/γ . The electron, caused to oscillate or "wobble," emits radiation which, brought back to the laboratory frame by a Lorentz transformation, has a rather sharply peaked spectrum. Under desirable operating conditions, this peak occurs at a wavelength $\sim P/\gamma^2$, and the width of the peak depends inversely on the number of periods in the wiggler. It would appear that a hundredfold increase in flux over that in the normal synchrotron radiation spectrum is achievable at the peak wavelength (*1*). Of course, this flux is radiated from an extended source and the total gain in flux is thus not available if fine refocusing is required. Magnetic periodicities P can be produced by magnets having bores of diameter approximately P . Since γ equals 1400 and 5000 for 0.7- and 2.5-GeV electrons, one obtains peak wavelengths of ~ 100 and ~ 10 Å, respectively, for a device with $P = 2$ cm. It should be mentioned, however, that injecting electrons into a high-energy, high-current storage ring which includes as an orbit element a wiggler 1 or 2 m long and 2 cm in bore has been likened to filling a thimble with a fire hose.

These wigglers are of interest not only because of their spectral characteristics but also because of the possibility of laser action in them. There has been an attempt at Stanford University (*2*) to induce laser action in such a device, in this instance not acting as an element of a storage ring but instead carrying an electron beam injected from an accelerator. Although the prospects for laser action seem good, all the answers are not yet in hand.

Many challenges are presented to the accelerator specialists who aim to design and build high-current, high-energy (GeV) storage rings endowed with orbit characteristics that result in high brightness and with other qualities that allow long lifetimes for the circulating current. If, in addition, long slim wiggler devices need to be incorporated, the level of challenge is further raised.

History

The fact that electrons, when accelerated, emit electromagnetic radiation has been appreciated since late in the 19th century. Toward the end of World War

II, electron energies in circular accelerators had reached the highly relativistic region and energy losses due to radiation became a matter of serious concern. Iwanenko and Pomeranchuk (3), followed by Blewett (4) and Schwinger (5), considered this question theoretically. Direct observation of the radiation came somewhat later, when G. N. Knowlton, using the then new 75-MeV synchrotron at the General Electric Research Laboratory, saw a brilliant light emitted tangentially from the electron orbit. Its properties and spectrum proved to be in accord with theory; this was confirmed in detail by measurements at numerous laboratories in subsequent years. In the late 1950's D. Tomboulion began to utilize synchrotron radiation for spectroscopy at the Cambridge Electron Accelerator (CEA). His death cut off this work, and it was only in the early 1970's, shortly before CEA was shut down, that synchrotron radiation research was revived there.

The first sustained research program involving synchrotron light was initiated in 1961 on the 180-MeV synchrotron, subsequently converted into a storage ring, at the National Bureau of Standards (NBS). This facility has been utilized by R. Madden and his associates primarily for atomic and molecular spectroscopy. By the middle 1960's, work was also being done at higher-energy synchrotrons in Italy, Germany, and Japan, where, despite the availability of hard radiation, it was largely limited to spectroscopy. At the University of Wisconsin, the 240-MeV storage ring, a by-product of a high-energy physics proposal, has become a national synchrotron radiation users' facility supported by the National Science Foundation (NSF). Inspection of Fig. 1 shows that its energy, like that of the NBS machine, limits its use to spectroscopic studies.

During the past few years research with synchrotron light has been growing explosively, as evidenced by the number of publications and the diversity of subjects studied. At this date there are more than 20 machines in several countries at which synchrotron light is being utilized. In every case either the operation is parasitic to a high-energy physics effort or it makes use of equipment originally designed and built for high-energy purposes. That is, these machines were not intended to have optimum optical characteristics as photon sources. Of the four extant facilities in the United States—Cornell, Stanford, NBS, and Wisconsin—the first two, at which photon use is parasitic, provide x-rays. Usage at Cornell has until now been limited to a num-

ber of faculty members; the photon laboratory at Stanford and the Wisconsin ring, however, operate as national facilities supported by the NSF.

Storage rings designed, constructed, and operated as dedicated synchrotron light sources are coming into being both here and abroad. We have come to value and make use of a phenomenon which, because it tended to limit the energy to which electrons could be accelerated, was in the past considered to be only vexatious.

Research and Technology:

Results and Prospects

As indicated in the foregoing section, research with ultraviolet synchrotron light is more highly developed than that with x-rays. Ultraviolet spectra from this source extend to much shorter wavelengths than are available from alternative sources; in fact, the ability to make spectroscopic measurements over a wide range of wavelengths, and hence to disengage the role of wavelength, was a first important benefit from the utiliza-

tion of synchrotron radiation. Research at shorter wavelengths, from say 100 Å to the hard x-ray region, is still largely in a developmental stage, although several techniques are coming into their own. A few examples of work in each wavelength region will be presented below. In some cases the research is merely an extension of existing techniques; in others, radical departures from standard methods have been made.

The ultraviolet. Much of the research with synchrotron radiation has been carried out at installations capable of producing photon spectra extending to wavelengths not shorter than 50 to 100 Å. Among the subjects encompassed by such ultraviolet investigations are bulk and surface electronic properties of metals and semiconductors, bonding and geometry of molecules adsorbed onto metals, absorption spectra and excited-state properties of gas molecules and their ions, and relaxation modes of excited states in complex organic solids and biologically interesting molecules. A few examples will serve to illustrate the special applicability of synchrotron radiation to this work.

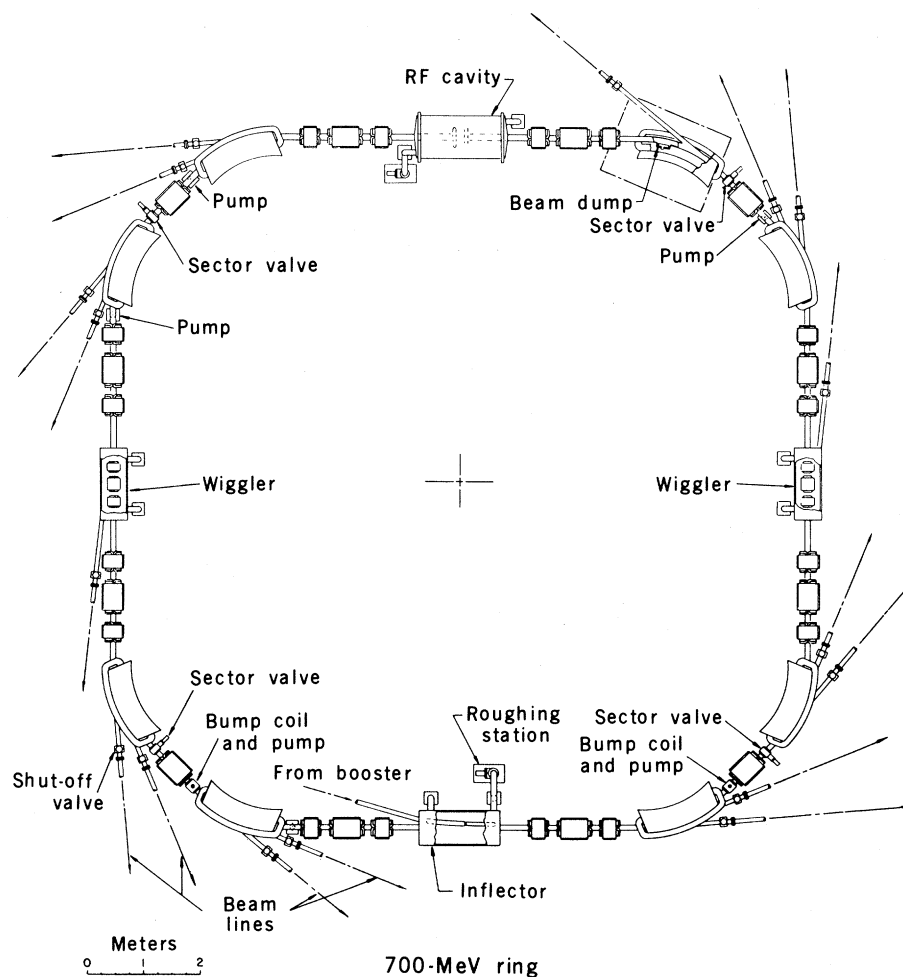


Fig. 2. General layout of a 0.7-GeV electron storage ring for production of ultraviolet and soft x-ray photons. A $2\frac{1}{2}$ -GeV x-ray source would be roughly three times larger in diameter.

Energy transfer in biomolecular systems is a subject of considerable interest. It has, for example, been known that the tryptophan chromophore split off from the native heme protein complex fluoresces strongly when excited by absorption at $\lambda \sim 2800 \text{ \AA}$; in the complex, however, the fluorescence of the tryptophan is two orders of magnitude weaker. This has been taken to mean that, in the combined form, the amino acid excitation is largely transferred to the heme group and is then dissipated by radiationless processes. A very short fluorescence lifetime would result from such heme quenching, and no attempt had been made to measure the lifetime until recently. In experiments carried out (6) at ACO, the 450-MeV Orsay storage ring near Paris, the weak fluorescence of the complex was measured at $\lambda > 3400 \text{ \AA}$, after excitation at $2800 \text{ \AA}$ by the ~ 2 -nanosecond pulses of synchrotron radiation. It was found, contrary to expectation, that at 3°C the hemoglobin lifetime is $\sim 3.5 \text{ nsec}$, only ~ 20 percent smaller than the free tryptophan lifetime at the same temperature. The hemoglobin lifetime is also quite temperature-sensitive, changing from the $\sim 3.5 \text{ nsec}$ at 3°C to $\sim 2.4 \text{ nsec}$ at 25°C . These results are interpreted as showing that, although about 99 percent of the excitation of the complex decays by radiationless transition, about 1 percent of the complex is in a configuration which deexcites in much the same way as the free tryptophan. This configuration, moreover, must survive for times greater than several nanoseconds and the rate at which it changes to a very fast quenching form appears to increase as the temperature is raised.

Although the spectroscopy and photochemistry of NO are classical subjects of study, important new information has come out of recent measurements made at ACO by d'Azy *et al.* (7) on low-lying vibronic states of NO. Intensities of absorption were compared with relative intensities among the same lines in fluorescence, as shown in Fig. 3. The peaks labeled A, B, C, and D in Fig. 3 correspond to different excited electronic states; the superscripts label vibronic levels, and the various rotational levels lie within each peak. Since, under the measurement conditions, the fluorescence intensities are nearly independent of pressure, the spectra shown in Fig. 3 demonstrate immediately that the C^0 and C^1 levels are strongly depopulated by unimolecular nondirect or radiationless processes (compare the intensities of these lines in the fluorescence spectrum with their intensities in the absorption

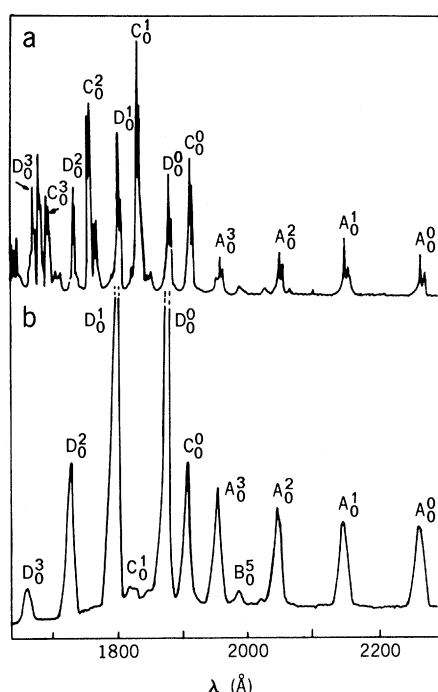


Fig. 3. Low-resolution absorption (a) and fluorescence (b) spectra of NO. Letters A, B, C, and D designate different excited electronic states; superscripts indicate vibrational levels. Note the different relative intensities of peaks C and D in the two spectra.

spectrum). To gain insight into depopulation mechanisms, the collision-free lifetimes and self-quenching rate constants were measured for all the levels shown. Perhaps the most interesting results are those for C^0 , whose envelope of rotational levels was scanned by excitation separately with narrow-band ($\Delta\lambda \sim 1.5 \text{ \AA}$) monochromatized radiation and with broad-band illumination. Three components were observed in decay: one was long-lived, corresponding to a $C \rightarrow A \rightarrow$ electronic ground state cascade; the second, shorter-lived and pressure-dependent, had a lifetime $\tau \sim 20 \text{ nsec}$ in the collision-free limit; and the third component, pressure-independent to 1 torr, had the shortest period, $\tau \sim 3 \text{ nsec}$. A study of these components as the rotational levels were scanned across the C^0 peak of Fig. 3 showed that their individual lifetimes remained constant but their relative intensities varied widely. The ratio of the integrated intensities of the 20- and 3-nsec components in the C^0 peak is plotted against exciting wavelength in Fig. 4; the variation is due mainly to that in the 20-nsec component, and the minima in the ratio occur in the high-frequency tails of rotational subbands. D'Azy *et al.* concluded that, at room temperature, about one-third of the excited molecules are pumped into low, long-lived rotational levels. This observation, together with an estimate of the

quantum yield for the dissociation process $\text{NO} \rightarrow \text{N} + \text{O}$, allowed them to obtain an "average lifetime" of the C^0 level in the upper atmosphere of ~ 10 to 15 nsec . This is almost an order of magnitude larger than the results of calculations based on estimated oscillator strengths and predissociation probabilities. It suggests that the concentration of NO in the earth's upper atmosphere is an order of magnitude greater than previously supposed.

A synchrotron radiation source is especially suited to fluorescence experiments, such as those described for hemoglobin and NO, because of the characteristic nanosecond photon pulse length and the high intensity and high degree of collimation in the beams. It is also advantageous that the high brightness makes narrow-band monochromatization feasible.

One widely used method for studying the surface and bulk electronic structure of solids has been photoelectron spectroscopy. Both the wavelength selectability and the polarization of synchrotron light have proved to be important for disentangling the effects of final state configurations and of transition probabilities.

Wagner and Spicer (8) at Stanford and Eastman and Grobman (9) at Wisconsin have studied the properties of the (111) surface of silicon (10). Figure 5 shows the photoelectron spectra obtained at two photon energies. The abscissa, initial state energy, is obtained by subtracting the photon energy from the electron kinetic energy, and it has been set so that the Fermi level is at zero. Several factors—for one, structure in the continuum states above the Fermi level to which the electrons are excited—are acting to produce the differences between the two spectra. Silicon, being a semiconductor, should not have bulk electronic states in the immediate vicinity of the Fermi level. The peak near -1 eV is therefore expected to be characteristic of the surface rather than the bulk, and this was shown to be the case by exposure of the crystal to 10^{-3} torr-sec of oxygen. Surface chemical oxidation caused the peak to disappear, giving the dashed spectrum in the -1-eV region in Fig. 5 and leaving the remainder of the curves, representing the bulk structure, unchanged.

With the power to measure photoemission as a function of the directions of the incident photons, the photon polarization, and the ejected electrons, it is possible to obtain information about the geometry as well as the energy of the system studied. Smith *et al.* (11) studied the

photoemission spectra of CO chemisorbed on the (001) face of Ni and of the clean Ni face itself. They obtained spectra at discrete electron emission angles at several photon energies under two different photon polarization conditions: with the electric vector parallel to the crystal face (*s* polarization), and with the electric vector nearly perpendicular to it (*p* polarization). The results are shown in Fig. 6 for 28-eV photons. The well-known large peak near the Fermi level (initial energy 0 eV) in the curves for clean Ni arises from the Ni *d* bands. Exposure to 3×10^{-6} torr-sec of CO resulted in the effects seen in the other four spectra, notably the appearance of peaks 1 and 2 at initial energies -8 and -11 eV. These are easily recognized from other work as being derived from the CO orbitals $1\pi + 5\sigma$ and 4σ , respectively. Some observations on the 4σ peak, which appears to be relatively unperturbed by the Ni, are especially interesting. At photon energies less than 40 eV, this peak appears at a normal angle of emission ($\theta_p = 0$) with *p* but not with *s* polarization. It appears under both polarizations at nonnormal emission angles and (not shown in Fig. 6) it is azimuthally isotropic when the crystal face is rotated about its normal. Smith *et al.* compared the angle- and polarization-dependent results for the 4σ and $1\pi + 5\sigma$ peaks with theoretical calculations for various orientations of CO on the Ni surface. They concluded that the axis of the chemisorbed CO molecule is perpendicular to the Ni face with the carbon atom next to the surface.

Soft x-ray lithography and microscopy. With respect to technique itself, lithography and microscopy are being carried out with soft x-rays at wavelengths of 10 to 20 Å (12). In this wavelength region there is no substitute for a synchrotron source. The specimen to be viewed microscopically is placed over a supporting wafer coated with an x-ray resist and illuminated as indicated in Fig. 7. After development in a solvent, the photoresist image is shadowed by heavy-metal evaporation and is viewed with a scanning electron microscope. Resolutions approaching 50 Å have been achieved and resist exposure times of 1 second appear practicable. For x-ray lithography, a mask in the desired design is imaged in the resist. A section of a Fresnel zone plate, so manufactured, is shown in Fig. 8. Sharply cut sub-micrometer structure, in which the depths of the cuts are greater than their widths, has been produced. Photons with wavelengths of about 10 to 20 Å are desirable because they are strongly ab-

sorbed in even very thin masks and thus provide great contrast on the resist. The high collimation of the synchrotron source reduces penumbral blurring.

If x-ray "lenses" can be made, this technology can be carried further. E. Spiller is endeavoring to develop multilayer materials to act as half-wave plates. There would be strongly reflect-

ing material at the nodes of the standing x-ray wave and weakly absorbing sandwich material between them. The reflectors are limited to the nodes, at which no absorption can occur, because good reflectors are also strong absorbers of the soft x-rays in question. If the dream of an x-ray microscope with focusing x-ray optical elements were realized, the steps of

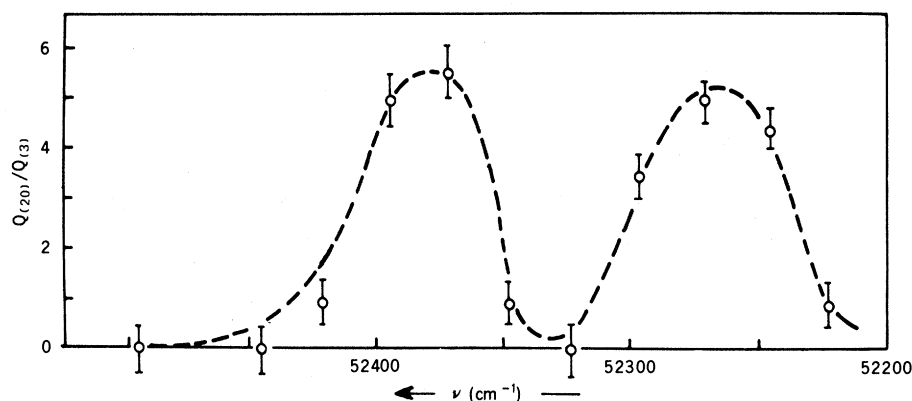


Fig. 4. Ratio of the intensity of the ~ 20 -nsec fluorescent decay to that of the ~ 3 -nsec decay in the C_0^0 line of NO. The scan is across the rotational levels lying within the C_0^0 peak of Fig. 3b. The abscissa is wave number.

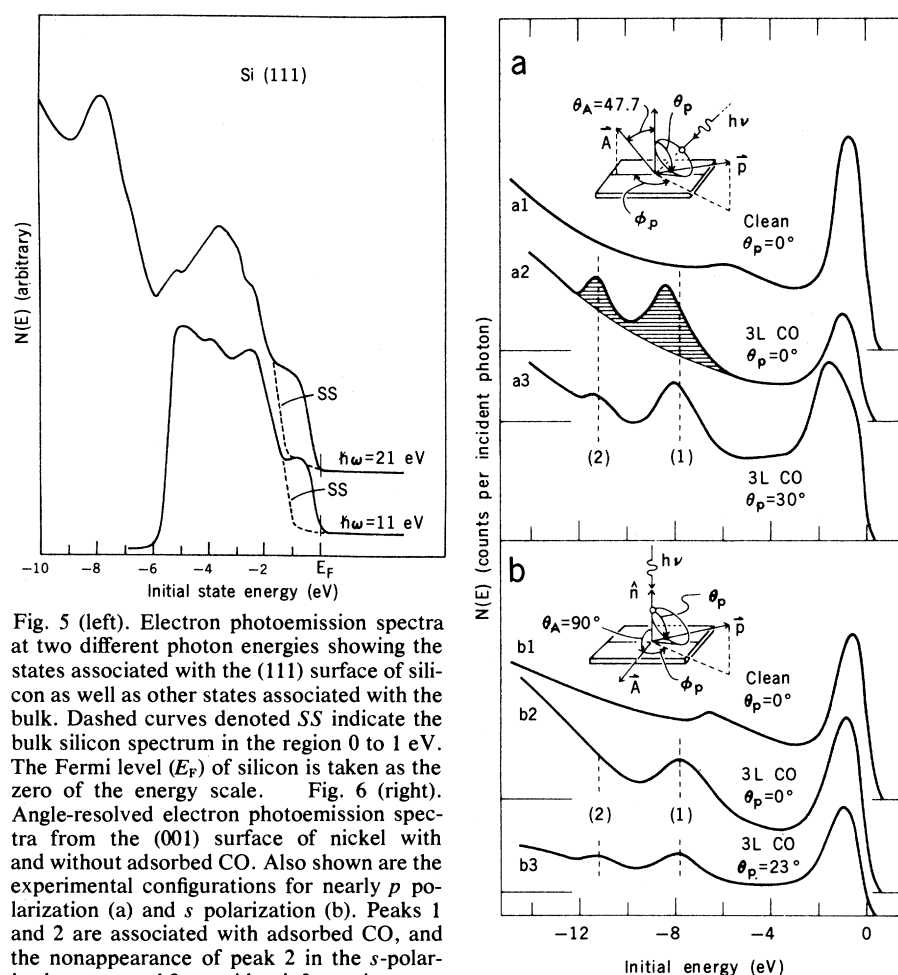


Fig. 5 (left). Electron photoemission spectra at two different photon energies showing the states associated with the (111) surface of silicon as well as other states associated with the bulk. Dashed curves denoted SS indicate the bulk silicon spectrum in the region 0 to 1 eV. The Fermi level (E_F) of silicon is taken as the zero of the energy scale. Fig. 6 (right). Angle-resolved electron photoemission spectra from the (001) surface of nickel with and without adsorbed CO. Also shown are the experimental configurations for nearly *p* polarization (a) and *s* polarization (b). Peaks 1 and 2 are associated with adsorbed CO, and the nonappearance of peak 2 in the *s*-polarized spectrum b2 provides information concerning the orientation of the adsorbed CO. In the diagram $\vec{p}$ is the momentum of the exiting electron; the detailed relations between the entering photon and the exiting electron are defined in (8-10).

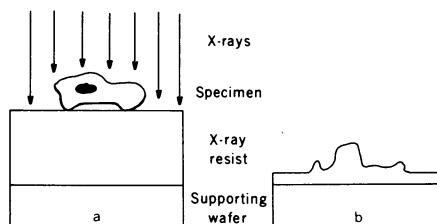
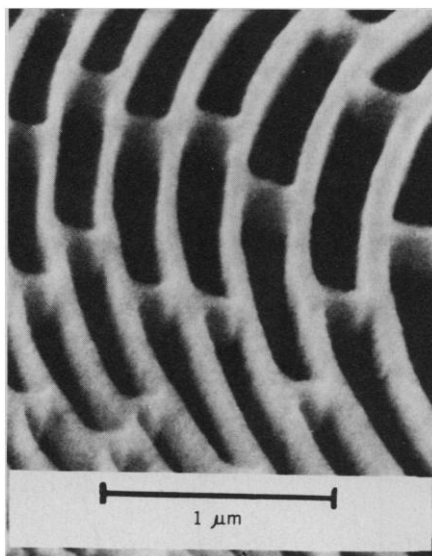


Fig. 7 (left). X-ray lithography and microscopy. (a) Irradiation of the x-ray resist through a specimen; (b) the image after development of the resist. For microscopy the replica is metallized and examined with a scanning electron microscope. In lithography, the resist is usually completely removed in the fully exposed areas opening these regions for etching and subsequent device fabrication. Fig. 8 (right). Section of a Fresnel zone plate fabricated by x-ray lithography. The electron synchrotron facility at Hamburg was used as the photon source. [Courtesy of E. Spiller, D. E. Eastman, and W. Grobman]



exposing, developing, shadowing, and microscopically scanning a resist would be eliminated. Although the resolution in this kind of microscopy is lower than that attainable in electron microscopy, there is greater sensitivity to structural detail in the interior of specimens and specimens are not restricted to a vacuum environment—wet samples may be studied. What is more, there is some range of x-ray wavelengths to choose from. By tuning to either side of the absorption edge of some constituent element, it may be possible to make difference micrographs showing enhancement of that element. Electron and x-ray microscopes would thus be complementary tools.

Other classes of microscopy have been the subject of some experimentation. Horowitz and Howell (13) devised a scheme wherein the sample is scanned with a tiny synchrotron radiation beam defined by a pinhole aperture and the fluorescent radiation from the specimen is measured with an energy-sensitive detector. Micrometer-scale quantitative analysis may be feasible with such a technique.

X-rays. Among the first x-ray experiments carried on at the Stanford storage ring were studies in which the phenomenon of extended x-ray absorption fine structure (EXAFS) was utilized. It has been recognized since the 1920's that structure such as that shown in Fig. 9 is observed in the absorption spectrum of an atom in a molecule or a solid but not in the spectrum of a free atom. A continuum x-ray source is required to obtain these data; unfortunately, the flux of bremsstrahlung from an x-ray tube is so low that the measurements are ordinarily difficult to make. With synchrotron radiation one can obtain a usable flux

10^5 to 10^6 times that from an x-ray tube.

The oscillatory character of the absorption probability, which extends well beyond the critical edge, is associated with the environment of atoms surrounding the absorbing site. The core electron, excited by absorption of the x-ray and emitted as an outgoing wave from the atom, is partially backscattered by the surrounding atoms. Photon absorption is enhanced if the backscattered electron wave and the outgoing wave are in phase at the absorbing atom, with a resulting pileup of electron density there. This interference effect of the surroundings is of short range because the mean free path for inelastic scattering, which "loses" the electron for these purposes, is of the order of 5 or 10 Å. The result is that one has a probe for the radial distances from an atom to its near neighbors. Limited angular information can sometimes be obtained as well. The probe is specific to the element whose absorption edge is scanned. For the technique to be useful, the element should not be in different environments in the same substance since the spectrum would then be a simple sum of the spectra representing the several environments.

When the element of concern is at moderate concentration in the material under examination, very roughly several atoms or more per hundred, the spectrum is usually derived from a measurement of x-ray transmission, I/I_0 , as a function of photon energy. The EXAFS measurements made by detecting the x-ray fluorescence associated with absorption, rather than the absorption itself, allow the study of atoms at dilutions characteristic of metal sites in biomolecules or of atoms present as trace constituents in solids. A variant of the fluorescence

detection is detection of the Auger electrons. Because these electrons have inelastic scattering mean free paths in solids which are of the order of 10 Å, EXAFS with Auger detection should be a useful technique for the study of structure in surfaces.

Figure 9 shows the EXAFS absorption spectrum of Fe in hemoglobin together with the spectra of Ni and Cu in two well-understood model compounds (14). These spectra are similar because the local environments of the metal atoms are similar; the small differences among the spectra are associated with actual differences in these environments. Oxy-, deoxy-, and carboxyhemoglobins from various sources are being studied in a number of EXAFS investigations at Stanford. Iron electronic configurations, iron ligand-atom distances, and ligand geometries are being examined. Information about the oxidation state of an absorbing species can be obtained by measuring the position in energy of the absorption edge. These data, too, are being employed in the hemoglobin work. Several EXAFS studies have centered on the iron-sulfur protein rubredoxin. Here, the original crystallographic study (15) indicated that of the four sulfur atoms surrounding the iron, three are at equal distances of ~ 2.3 Å while the fourth is at 2.05 Å. The question arose whether the abnormally short Fe-S bond is essential to the chemistry of this protein. Later EXAFS studies showed convincingly (16) that the four bond lengths are equal within 0.1 Å, and further analysis of the crystallographic data yielded results confirming this finding. This shows how EXAFS, in providing distances of near-neighbor atoms from an identified constituent atom, can make powerful contributions to the crystallography of complicated structures with large unit cells. Such data simplify the search for solutions of diffraction patterns.

Although it is implied in the foregoing discussion, it should be pointed out that the EXAFS method is not limited to structures in ordered crystalline arrangement. Amorphous structures and molecules in solution are amenable to study. Structural parameters can be determined for, say, metalloproteins in a solution corresponding to a functional environment; distances between metal ions and water molecules in their hydration spheres have been measured. There is much to be learned by use of the technique.

The application of synchrotron radiation to EXAFS was pioneered by S. W. Lytle, E. A. Stern, and D. E. Sayers; subsequently, investigators from Bell

Laboratories did much to provide the method with a firm quantitative basis. Near-neighbor distances can sometimes be determined to 0.01 Å.

The high brightness and the nature of the synchrotron radiation spectrum, which allows choice of optimum wavelength, have been employed at Hamburg in low-angle diffraction studies of muscle. One is here concerned with the organization of biological material having periodicities of the order of hundreds of angstroms. In these studies (17) it was observed that adenosine triphosphate analogs at high concentrations produce a "relaxed" state in the tissue structure but that at low concentrations there is a distinct state intermediate between rigor and relaxation which is not simply a mixture of the two. Low-angle studies of biological membranes and their states in the presence of various divalent cations (such as Ca^{2+} and Zn^{2+}) are also of current interest.

In England, advantage has been taken of the high source brightness for topographical studies of small imperfections in nearly perfect crystals and of the organization of domains and of defects in crystalline samples.

In the case of some substances whose structures one would wish to determine, it has not been possible to grow crystals sufficiently large for standard crystallographic diffraction methods. Such substances, with crystals of dimensions perhaps less than 0.1 mm, should be usable with a synchrotron source because of its high brightness. This should be especially helpful for a number of biological materials.

What may be the most tantalizing prospect for x-ray crystallography is the use of wavelength variation to attack the phase problem. From a single x-ray pattern one cannot determine the phase of the scattering of one atom relative to that of another. This information, needed for the solution of complicated structures with many atoms per unit cell, is generally obtained in biomolecular crystallography by the method of isomorphous substitution; the atom normally occupying some site is replaced by another of different atomic number. The resulting change in scattering assists in phase determination, which can generally be done by the use of two or more similarly substituted crystals. Alternatively, and perhaps much more conveniently, one could change the scattering markedly by changing the x-ray wavelength across the characteristic x-ray absorption edge of a constituent atomic species. With a synchrotron source this effect could be employed by tuning to photon energies

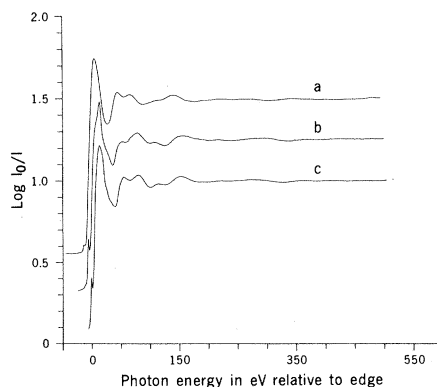


Fig. 9. Extended x-ray absorption fine structure (EXAFS) spectra of the *K* edges of three metallo-organic complexes. (a) Spectrum associated with the iron site in deoxyhemoglobin A, which is to be compared with spectra of two well-characterized model compounds, (b) nickel and (c) copper tetraphenylporphyrin. The three *K* edges have been brought to a common zero for ease of comparison. The characteristic interference pattern resulting from photoelectron scattering by the first shell of nitrogens and by the α -pyrrole carbons is clearly visible in all three spectra.

just below and then just above the edge, where there is strong anomalous scattering for the atom concerned. Scattering from other atoms would be essentially unaffected by such a wavelength change. Investigation of this technique is in an early stage, and its usefulness in practice remains to be established.

As is often the case when new tools become available, synchrotron light is stimulating the invention of new techniques and the revival of some old ones that have fallen into disuse. There has, for example, been some experimentation in single-crystal and powder diffraction (18) and in small-angle scattering from large-spaced structures with the full continuous spectrum of the source incident on the specimen; the wavelengths of the x-rays scattered at a fixed angle are ascertained with an energy-sensitive detector. This turns out to be a comparatively simple, rapid measurement. Potentially very powerful is the application of synchrotron light to the diffraction study of time-dependent structure on biological or physical time scales. Low-angle diffraction studies of the action of enzymes in solution have been proposed at Hamburg, and we have heard that diffraction snapshots at several-millisecond exposure times have been taken in the Soviet Union. Retinal function, metal fatigue and fracture, and phase transitions are examples of phenomena whose dynamics may be amenable to such study.

Technology. The foregoing discussion of research applications is certainly incomplete; it is nevertheless clear that the areas in which the work can be advanced

by use of a synchrotron source reach from frontier science to technology. A few predominantly technological uses, some potential and others actual, will give some picture of the possibilities in this domain.

Information about the chemical states and local environments of pollutant elements found in atmospheric samples is needed if one is attempting, with control in view, to understand the operations of pollution sources and dispersal mechanisms. Photoelectron spectroscopy and EXAFS come to mind here. On a somewhat different front, at the Stanford facility a cell has been used with which one can make EXAFS measurements of the catalytically active atoms in a catalyst composite during the course of reaction. This type of investigation is exciting industrial interest.

Some of the processes of energy production and metabolism in biological systems involve chemically active heavy atoms. Preliminary EXAFS studies have been made of the active molybdenum sites in nitrogenase, the enzyme in plant bacteria that catalyses the fixation of atmospheric nitrogen. If it were possible to model this process in some nonenzymatic way, one might be able to reduce the large expenditure of energy now required for the production of synthetic ammonia for fertilizers. Biosystems may play an increasingly important role in our energy economy, and synchrotron light should prove useful for research into their properties.

Striking results have been achieved with soft x-rays for lithography and microscopy, as exemplified in Fig. 8. The electronics industry produces integrated circuits whose size is steadily shrinking and whose characteristic dimensions may soon approach those shown in Fig. 8. Electron beam lithography, which is currently used, has certain advantages over the technique of exposure to ultraviolet or x-ray photons through a mask—it is easy, for example, to superimpose patterns. On the other hand, because of electron scattering, electron beam lithography produces detail which tends to be less sharp than that obtainable with soft x-rays. One can expect that the demand for electronic and optical structures on the submicrometer scale will greatly increase, and x-ray and electron lithography should provide complementary means for satisfying it.

We are entering a period of exponential growth of research made possible by an unusual kind of photon generator, a spin-off from accelerator development in high-energy particle physics. A lively evolution in experimental tech-

niques is taking place, and new information is already yielding fresh insights into chemical, physical, and biological systems.

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Diversity in Tropical Rain Forests and Coral Reefs

High diversity of trees and corals is maintained only in a nonequilibrium state.

Joseph H. Connell

The great variety of species in local areas of tropical rain forests and coral reefs is legendary. Until recently, the usual explanation began with the assumption that the species composition of such assemblages is maintained near equilibrium (1). The question thus became: "how is high diversity maintained near equilibrium?" One recent answer

communities is a consequence of past and present interspecific competition, resulting in each species occupying the habitat or resource on which it is the most effective competitor. Without perturbation this species composition persists; after perturbation it is restored to the original state (3).

In recent years it has become clear

forces, often abrupt and unpredictable, set back, deflect, or slow the process of return to equilibrium (4). If such forces are the norm, we may question the usefulness of the application of equilibrium theory to much of community ecology.

In this article I examine several hypotheses concerning one aspect of community structure, that is, species richness or diversity (5). I first explore the view that communities seldom or never reach an equilibrium state, and that high diversity is a consequence of continually changing conditions. Then I discuss the opposing view that, once a community recovers from a severe perturbation, high diversity is maintained in the equilibrium state by various mechanisms.

Here I apply these hypotheses to organisms such as plants or sessile animals that occupy most of the surface of the land or the firm substrates in aquatic habitats. I consider two tropical communities, rain forests and coral reefs, concentrating on the organisms that determine much of the structure, in these cases, trees and corals. Whether my arguments apply to the mobile species, such as insects, birds, fish, and crabs, that use these structures as shelter or food, or to nontropical regions, remains to be seen. I deal only with variations in diversity within local areas, not with large-scale geographical gradients such as tropical to temperate differences. While the hypotheses I present may help explain them, such gradients are just as likely to be produced by mechanisms not covered in the present article (6).

Various hypotheses have been proposed to explain how local diversity is produced or maintained (or both). I have reduced the number to six, which fall into two general categories:

Summary. The commonly observed high diversity of trees in tropical rain forests and corals on tropical reefs is a nonequilibrium state which, if not disturbed further, will progress toward a low-diversity equilibrium community. This may not happen if gradual changes in climate favor different species. If equilibrium is reached, a lesser degree of diversity may be sustained by niche diversification or by a compensatory mortality that favors inferior competitors. However, tropical forests and reefs are subject to severe disturbances often enough that equilibrium may never be attained.

for tropical bird communities is given as follows: "The working hypothesis is that, through diffuse competition, the component species of a community are selected, and coadjusted in their niches and abundances, so as to fit with each other and to resist invaders" (2). In this view, the species composition of tropical

that the frequency of natural disturbance and the rate of environmental change are often much faster than the rates of recovery from perturbations. In particular, competitive elimination of the less efficient or less well adapted species is not the inexorable and predictable process we once thought it was. Instead, other

Joseph H. Connell is a professor of biology at the University of California, Santa Barbara 93106.