

Introduction: X-rays in Chemistry

It has been slightly over a century since Röntgen discovered the existence of a novel form of radiation that he referred to as X-rays. Although the first practical uses of X-rays were medical, it did not take long for X-rays to become an important tool across the scientific spectrum. A crucial development occurred in 1912 when von Laue and co-workers performed the experiments that proved at the same time that X-rays are electromagnetic radiation and that crystals consist of three-dimensional periodic arrays of scattering matter. In the last 100 years, at least 16 Nobel Prizes have been based either on explaining the interactions of X-rays with matter or on using these interactions to solve important scientific problems. This issue of *Chemical Reviews* documents the crucial role that X-rays now play across the field of chemistry.

Like all electromagnetic radiation, X-rays can do only two things of interest when they interact with matter: they can be scattered or absorbed (the transmission of X-rays unperturbed being of little interest). The unique ability of X-rays to answer chemical questions is a consequence of the size of X-ray wavelengths, which are typically about 10 pm (1 Å), corresponding to an energy of ca. 12 keV. Since these wavelengths are comparable to the size of an atomic bond, X-ray scattering (or, for samples with long-range periodicity, X-ray diffraction) gives information about the size and shape of molecules. Similarly, X-ray energies are comparable to core-electron binding energies. This means that X-ray absorption (and the subsequent re-emission of X-ray fluorescence) can be used to probe core electron energies. Core-electron binding energies are, to a first approximation, dependent only on the atomic number of the absorbing atom. Consequently, X-ray absorption and X-ray fluorescence are almost unique among spectroscopic methods in providing atom-specific spectral data. This can be used for elemental analysis or for selectively studying a single element in a complex mixture.

Because X-rays have been known since 1895, and the basic physics of X-ray absorption and X-ray scattering has been understood since the 1920s, X-ray methods can reasonably be described as mature. Nevertheless, X-ray studies have experienced a true renaissance over the last decade. This is primarily

due to the deployment over that time period of a new generation of powerful X-ray synchrotron sources. Conventional X-ray tubes, of the sort that Röntgen built, produce intense "characteristic" X-ray lines but have relatively weak continuum emission. In contrast, modern X-ray synchrotron sources can produce intense X-ray emission with a nearly flat spectral distribution over the chemically interesting range of X-ray energies. The total flux available from a synchrotron exceeds that of a conventional X-ray tube by perhaps 6 orders of magnitude. The enhancement provided by synchrotron sources is even more dramatic if one considers the flux density (that is, the number of photons that can be focused onto a small sample such as a crystal). Here, synchrotron sources outperform conventional sources by 10 or more orders of magnitude. This tremendous increase in capability has made possible experiments that were only dreams a decade ago. Accordingly, at least 7 of the 10 articles in this issue describe experiments that are crucially dependent on the availability of synchrotron radiation.

In any *Chemical Reviews* thematic issue there are inevitable omissions due to space and other constraints. One can easily identify numerous other areas that could have been, but are not, included. These include both powder diffraction, where the extraordinary resolution of synchrotron beamlines has greatly extended the capabilities of powder diffraction for structure solution, and diffraction-based studies of reactions in crystals (although the related topic of time-resolved biochemical crystallography is discussed). Several additional aspects of X-ray absorption spectroscopy could have been discussed, including circular dichroism and magnetic circular dichroism, polarization-dependent X-ray absorption, time-resolved X-ray absorption, and recent advances in the theoretical descriptions of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Several methods that depend on the coherent interference of X-rays could have been included, including studies of X-ray photon correlation, of X-ray standing waves, and of the use of X-ray phase-contrast in imaging (including very interesting recent applications of interference contrast to significantly enhance the information content of medical X-ray imaging).

Finally, we could have included a discussion of some of the recent developments of X-ray methods for industrial applications, including X-ray microlithography, where the short wavelength of X-rays offers the possibility of extending device dimensions below the diffraction limit of UV lithography, and total reflection X-ray fluorescence, which is providing exquisite sensitivity for characterizing contamination in semiconductor substrates, with detection limits as low as 10^6 atoms/cm². All of these, and many others, are important and merit exposure in the prime scientific literature.

In addition to the omissions above, which were judged too new, having been recently reviewed elsewhere, or having so far had too little impact on chemistry, there are several further omissions that bear comment. We have specifically excluded "standard" X-ray methods such as X-ray fluorescence as a tool for elemental analysis, small molecule crystallography, and protein structure determination. This is not to indicate that these techniques are unimportant to chemistry. Rather, it is a reflection of their pervasive impact on chemistry—these are techniques that are so widely used that there exist numerous reviews and monographs describing their applications.

The 10 articles included in this issue can be broken down into two main categories, depending on whether they rely on scattering or absorption. In the area of X-ray scattering, much of the current interest has involved extending diffraction methods beyond the conventional limitation of determining static atomic positions in bulk solids. Moffat discusses the extension to time-resolved studies and shows how these can be used to deduce biochemical mechanisms. Koritsanszky and Coppens discuss extensions beyond atomic position, showing how X-ray diffraction can be used to probe electronic structure and lead to new insight in chemical bonding. Moulton and Zaworotko discuss the burgeoning field of crystal engineering, stimulated by the dramatic advances in structure analysis, that has led to a plethora of new supramolecular solids, giving new meaning to the concepts of isomerism and polymorphism. Chemical reactions, at least those involving solids, preferentially take place at surfaces. Two articles focus on the crystal interfaces and the use of X-ray measurements to characterize their structures. Leiserowitz and co-workers describe the structures of spontaneously formed crystalline films at the air–water interface, studies made possible by the advent of intense and highly collimated beams from synchrotron sources, while Ward shows how X-ray diffraction can be combined with atomic force microscopy to obtain pivotal information on organic surfaces. Articles by Chu and

Hsiao and by Doniach focus on noncrystalline diffraction. Chu and Hsiao show how small-angle X-ray scattering can be used to elucidate both the static structure and dynamics of polymers, while Doniach describes how time-resolved small-angle X-ray scattering is yielding new insights into the mechanism of protein folding. Two papers involve X-ray absorption. de Groot presents an overview of the use of high-resolution spectroscopy, both in absorption and in emission mode, to obtain detailed information on the electronic structure of the X-ray-absorbing atom. Bertsch and Hunter show how X-ray absorption and emission can be coupled in microfocus X-ray probes, thus providing a novel method for element-specific chemical imaging, with broad implications in earth and environmental sciences, biosciences, and the study of materials. Finally, the article by Hodeau and co-workers shows the advantages of bringing together absorption and diffraction in measuring the energy dependence of diffraction near an absorption edge. In this way, it is possible to capitalize on the strengths of both methods and achieve a chemical selectivity, which allows not only precise identification of different elements, even if occupying the same site, but also differentiation between different valence states of the same element in the sample.

As has been the case for other physical techniques in recent years, X-ray absorption and diffraction methods are currently being extended to include the time domain, not only in macromolecular and polymer studies, but also in other fields of direct chemical interest. As chemistry has been called the science of molecular change, such studies, on time scales ranging from hours down to nanoseconds and less, are highly relevant and may be expected to contribute greatly to our understanding of chemical processes at the atomic level. The projected construction of X-ray free-electron lasers (FEL), which will lead to an additional increase in X-ray intensity of several orders of magnitude, will enhance the power of such methods and make not yet envisioned experiments possible. It is clear that the importance of X-rays in chemistry is likely to grow and will justify additional thematic issues in coming years.

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