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STUART A. RICE

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

CONTENTS

TIME-RESOLVED X-RAY DIFFRACTION FROM LIQUIDS

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CONTENTS

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I. INTRODUCTION

Since the discovery of X-rays by Roentgen, X-ray diffraction has always been the major technique permitting the localization of atoms in molecules and crystals. Great scientists such as Bragg, Laue, and Debye made major contributions to its development. Atomic structures of many systems have been determined using this technique. These structures are actually known with a great accuracy, and one can hardly imagine a science without this information. The recent progress achieved using synchrotron sources of X-ray radiation are impressive.

However, systems with localized atoms represent only a first challenge. The next challenge is monitoring atomic motions in systems that vary in time. Following atomic motions during a chemical process has always been a dream of chemists. Unfortunately, these motions evolve from nanosecond to femtosecond time scales, and this problem could not have been overcome until ultrafast detection techniques were invented. Spectacular developments in laser technology, and recent progress in construction of ultrafast X-ray sources, have proved to be decisive. Two main techniques are actually available to visualize atomic motions in condensed media.

The first is time-resolved optical spectroscopy. The system is excited by an intense optical pulse, and its return to statistical equilibrium is probed by another pulse, which is also optical. Zewail and several other outstanding scientists contributed much to its development. For textbooks describing it, see Refs. 1–4. The second technique comprises time-resolved X-ray diffraction and absorption. The excitation of the system is optical as before, but the probing is done using an X-ray pulse. Long range order may be probed by diffraction, whereas short range order may be monitored by absorption. Unfortunately, general literature is still scarce in this domain [5–7].

The major advantage of time-resolved X-ray techniques, as compared to optical spectroscopy, is that their wavelength λ as well as the pulse duration τ can be chosen to fit the atomic scales. This is not the case for optical spectroscopy, where the wavelength λ exceeds interatomic distances by three orders of magnitude at least. Unfortunately, X-ray techniques also have their drawbacks. They require large scale instruments such as the synchrotron. Even much larger instruments based on free electron lasers are actually under construction. The "nonhuman" size of X-ray instrumentation is sometimes an objection against the use of this method, whereas optical spectroscopy is free of this objection.

The purpose of this chapter is to review ultrafast, time-resolved X-ray diffraction from liquids. Both experimental and theoretical problems are treated. Section II describes the principles of a time-resolved X-ray experiment and details some of its characteristics. Basic elements of the theory are discussed in Sections III–V. Finally, Section VI presents recent achievements in this domain. The related field of time-resolved X-ray spectroscopy, although very promising, is not discussed.

II. EXPERIMENT

A. Basic Principles

The system under consideration is a liquid sample, either a pure liquid or a solution. It is pumped by a laser, which promotes a fraction of the molecules into one or several excited quantum states. The energy deposited by the laser diffuses into the system in one or several steps, generating several sorts of events. If the excitation is in the optical spectral range, chemical reactions may be triggered and the sample is heated. If it is in the infrared, only heating is generally present. The return of the excited system to thermal equilibrium is then probed using a series of time-delayed X-ray pulses (Fig. 1). The resulting diffraction patterns consists of circular rings, centered on the forward beam direction. Finally, the collection of diffraction patterns obtained in this way is transformed into a collection of molecular photographs; this step is accomplished by theory. A time-resolved X-ray experiment thus permits one to "film" atomic motions.

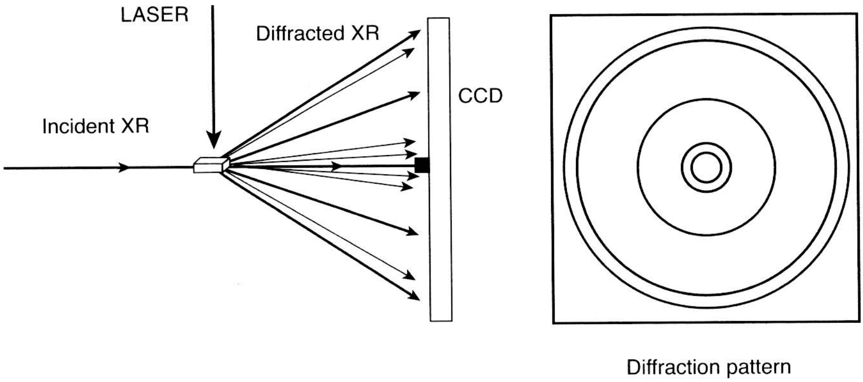

Figure 1. Time-resolved X-ray diffraction experiment (schematic). The liquid sample is excited by a laser pulse, and its temporal evolution is monitored by a time-delayed X-ray pulse. The diffracted radiation is measured by a charge-coupled detector (CCD). In practice, the laser and X-ray beams are not perpendicular to each other, but nearly parallel.

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This rough picture can be sharpened by providing some additional information. The experimental setup appropriate for time-resolved diffraction comprises a pulsed synchrotron source, a chopper that selects single X-ray pulses from the synchrotron, a femtosecond laser activating the process to be studied, a capillary jet, and an integrating detector measuring the intensity of the scattered X-ray radiation. What is desired in reality is not the scattered X-ray intensity by itself, but the difference between scattered intensities in the presence or absence of the laser excitation. This difference intensity is very small and is thus particularly difficult to measure. The images must be integrated azimuthally and corrected for polarization and space-angle effects. How is this sort of experiment realized in practice? Some major points are discussed next [5–8]. For new trends in instrumentation, see Refs. 9–11.

B. Practical Realization

1. X-Ray and Optical Sources

The first and central point in this discussion concerns the pulsed X-ray source. The shortest time scales involved when chemical bonds are formed or broken are on the order of a few femtoseconds. An ideal X-ray source should thus be capable of providing pulses of this duration. Unfortunately, generating them represents a heavy technological problem. The best one can do at present is to use a pulsed synchrotron X-ray source (Fig. 2). Electrons are rapidly circulating in a storage ring at speeds close to the speed of light. X-rays are spontaneously emitted longitudinal to the orbit. This emission is amplified in so-called straight sections,

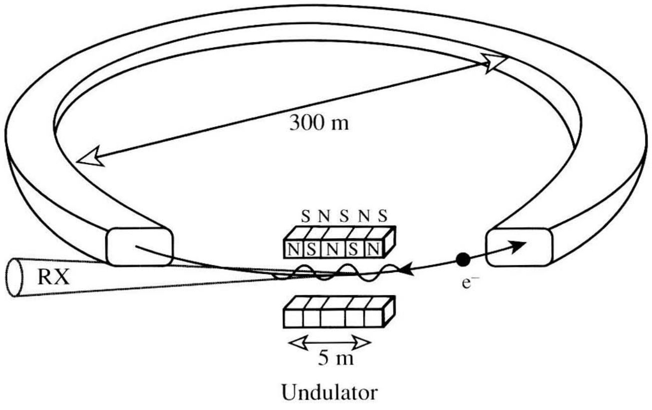

Figure 2. Synchrotron X-ray source (schematic). The electron execute circular motions in the storage ring and emit intense X-rays along the tangent of the orbit. This radiation is enhanced by undulator magnets that are often placed inside the vacuum vessel for enhanced performance. The storage ring has a number of straight sections for undulators and wigglers (not shown).

where a sinusoidal motion is imposed on the electrons by undulator magnets. The X-rays emitted from successive bends interfere and enhance the radiation. A bunched electron beam then produces an intense X-ray radiation with 100 ps X-ray pulses. Unfortunately, subpicosecond X-ray pulses cannot be generated in this way. There is a gap between what is possible at present and what is needed. Facilities based on the use of free electron lasers are under construction to bridge this gap.

Sources of optical radiation are much more conventional. One generally employs commercially available lasers, generating 100 fs pulses with pulse energy between 10 and 100 μJ. These lasers run in phase with the chopper. The power density of the optical beam on the sample is typically on the order of 10 GW/mm^2. The time lag between the X-ray and optical pulses is controlled electronically by shifting the phase of the oscillator feedback loop with a digital delay generator. The short time jitter in the delay is on the order of a few picoseconds, but at long times it increases to tens of picoseconds. The angle between the X-ray and laser beam is 10 degrees, making the excitation geometry near collinear.

2. *Detectors*

Several detection techniques have been developed. In the first of them, the scattered X-rays are intercepted by a phosphor screen, which transforms them into optical photons. The latter are then channeled by optical fibers to a charge-coupled detector (CCD). In this detector the vast majority of X-ray photons are registered. However, it is not a straightforward method to measure very small relative changes in the CCD signal. The detection should be strictly linear in the photon number, which is not easy to achieve in practice. Finally, the X-ray dose must be kept constant during data collection. The exposure must thus be prolonged to compensate for the decaying synchrotron current. Another very different detection technique consists of using streak cameras. The incident X-ray pulse is transformed into an electronic pulse, which is "streaked" by an electrostatic field onto a CCD. Although there are streak cameras with picosecond time resolution, they require very high X-ray intensities and are therefore of limited use. There is no perfect detector, all have strengths and weaknesses, and the optimum choice depends on the exact nature of the measurements.

3. *Data Reduction Procedures*

As emphasized earlier, the weakness of the difference intensity is a specific difficulty with this sort of experiment. The ratio between the difference and the full scattering intensity is on the order of 10^{-2}–10^{-4}. This is particularly problematic in solution work, where the radiation scattered by the solute is buried in that from the solvent. A further complication arises from the interference between X-ray and optical manipulations. In fact, the intensity of

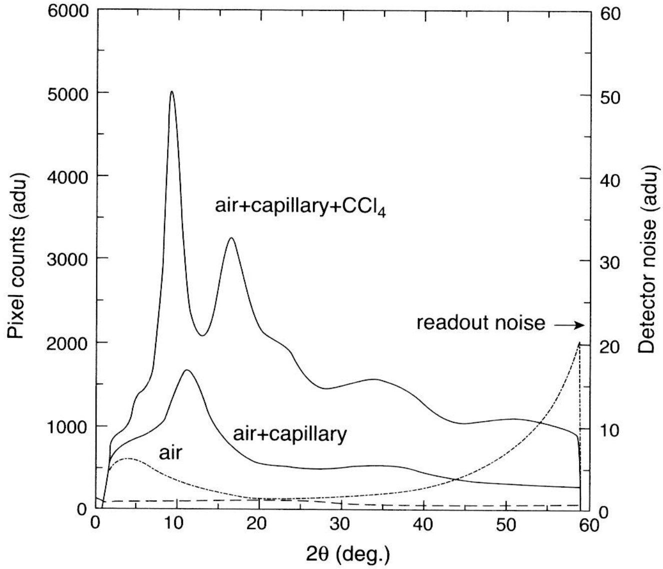

Figure 3. Various contributions to the scattered X-ray intensity. The system under consideration is a dilute I_2/CCl_4 solution.

the difference radiation depends on the number of excited molecules, which in turn is a function of the solute concentration. If the system is excited with ultrashort optical pulses, this number should not exceed a critical system-specific level. If this restriction is not respected, multiphoton absorption may be activated in the solute and solvent, and this may obscure the interpretation. In practice, the concentration of excited species is thus always very low, typically $\frac{1}{1000}$. Once again, the intensity of the X-ray beam is all important.

Another specific difficulty in X-ray experiments is that diffraction images contain contributions not only from the liquid sample but also from the capillary and air. It is often delicate to disentangle these contributions from each other (Fig. 3). Note that the main noise in the difference signal comes from the photon statistics in the X-ray background. This is an intrinsic limitation in solution phase ultrafast X-ray scattering. One must also take into account the presence of radioactivity and cosmic rays. The parasitic counts generated by these two mechanisms may be eliminated by subtracting two images, the original minus 180° rotated.

All measured intensities can be put on absolute scale by proceeding as follows. At high angles the scattering pattern can be considered as arising from a collection of noninteracting gas molecules rather than from a liquid sample. The Compton scattering cannot be neglected, but it is independent of molecular structure. Then, fitting experimental data to formulas from gas phase theory, the concentration of excited molecules can be determined. Another problem is that the undulator X-ray spectrum is not strictly monochromatic but has a slightly asymmetric lineshape extending toward lower energies. This problem may be handled in different ways, for example, by approximating its spectral distribution by its first spectral moment [12].

III. THEORY

A. Generalities

The first theoretical attempts in the field of time-resolved X-ray diffraction were entirely empirical. More precise theoretical work appeared only in the late 1990s and is due to Wilson and co-workers [13–16]. However, this theoretical work still remained preliminary. A really satisfactory approach must be statistical. In fact, macroscopic transport coefficients like the diffusion constant or the chemical rate constant break down at ultrashort time scales. Even the notion of a molecule becomes ambiguous: At which interatomic distance can the atoms A and B of a molecule A–B be considered to be free? Another element of consideration is that the electric field of the laser pump is strong and its interaction with matter is nonlinear. What is needed is thus a statistical theory reminiscent of those from time-resolved optical spectroscopy. A theory of this sort has been elaborated by Bratos and co-workers [17–19].

An important specific feature of the present experiment is worth noting. The X-ray photons have energies that are several orders of magnitude larger than those of optical photons. The pump and probe processes thus evolve on different time scales and can be treated separately. It is convenient to start with the X-ray probing processes and treat them by Maxwellian electrodynamics. The pumping processes are studied next using statistical mechanisms of nonlinear optical processes. The electron number density $n(\mathbf{r},t)$, supposed to be known in the first step, is actually calculated in this second step.

We shall now focus our attention on spatially isotropic liquids. The key quantities of the theory are as follows. An intense optical pulse of frequency Ω_O brings it into an appropriate initial state. τ seconds later, an X-ray pulse of frequency $\Omega_X \gg \Omega_O$ hits the sample and is then diffracted by it. What one measures is the difference signal $\Delta S(\mathbf{q}, \tau)$, defined as the time-integrated X-ray energy flux $S(\mathbf{q}, \tau)$ scattered in a given solid angle in the presence of the pump, minus the time-integrated X-ray energy flux $S(\mathbf{q})$ in the same angle in the absence of the pump. It depends on two variables: the scattering wavevector $\mathbf{q} = \mathbf{q}_r - \mathbf{q}_s$, where $\mathbf{q}_r$ and $\mathbf{q}_s$ are wavevectors of the incident and the scattered X-ray radiation, respectively, and the time delay τ between pump and probe. $\Delta S(\mathbf{q}, \tau)$ is the main quantity to be examined in what follows.

B. Maxwellian Description of X-ray Probing

The Maxwell theory of X-ray scattering by stable systems, both solids and liquids, is described in many textbooks. A simple and compact presentation is given in Chapter 15 of the Landau–Lifshitz volume, *Electrodynamics of Continuous Media* [20]. The incident electric and magnetic X-ray fields are plane waves $\mathbf{E}_X(\mathbf{r},t) = \mathbf{E}_{X0}\exp[i(\mathbf{q}_I\mathbf{r} - \Omega_X t)]$ and $\mathbf{H}(\mathbf{r},t) = \mathbf{H}_{X0}\exp[i(\mathbf{q}_I\mathbf{r} - \Omega_X t)]$ with a spatially and temporally constant amplitude. The electric field $\mathbf{E}_X(\mathbf{r},t)$ induces a forced oscillation of the electrons in the body. They then act as elementary antennas emitting the scattered X-ray radiation. For many purposes, the electrons may be considered to be free. One then finds that the intensity $I_X(\mathbf{q})$ of the X-ray radiation scattered along the wavevector $\mathbf{q}$ is

$$I_X(\mathbf{q}) = \left(\frac{e^2}{mc^2}\right)^2 \sin^2\phi I_{0X} f^*(\mathbf{q}) f(\mathbf{q}) \qquad (1)$$

where I_{0X} is the intensity of the incident X-ray radiation, ϕ is the angle between $\mathbf{E}_X$ and $\mathbf{q}$, and $f(\mathbf{q}) = \int d\mathbf{r}\exp(-i\mathbf{q}\mathbf{r})n(\mathbf{r})$ is the Fourier-transformed electron number density $n(\mathbf{r})$; this latter quantity is generally termed a form factor. The success of this theory is immense; see the textbooks by Guinier [21], Warren [22], and Als-Nielsen and Morrow [23]. In ordered systems like crystals, it permits one to determine atomic positions, that is, to "photograph" them. In disordered systems like powders or liquids, the data are less complete but still remain very usable. A large variety of systems have been analyzed successfully using this approach.

How must this theory be modified to describe the effect of the optical excitation? The incident electric and magnetic X-ray fields are now pulses $\mathbf{E}_X(\mathbf{r},t) = \mathbf{E}_{X0}(t)\exp[i(\mathbf{q}_I\mathbf{r} - \Omega_X t)]$ and $\mathbf{H}_X(\mathbf{r},t) = \mathbf{H}_{X0}(t)\exp[i(\mathbf{q}_I\mathbf{r} - \Omega_X t)]$. They still are plane waves with a carrier frequency Ω_X, but their amplitudes $\mathbf{E}_{X0}(t)$ and $\mathbf{H}_{X0}(t)$ vary with time. The same statement applies to the electron density $n(\mathbf{r},t)$, which also is time dependent. However, these variations are all slow with time scales on the order of $1/\Omega_X$, and one can neglect $\partial\mathbf{E}_{X0}(t)/\partial t$ and $\partial\mathbf{H}_{X0}(t)/\partial t$ as compared to $i\Omega_X\mathbf{E}_{X0}(t)$ and $i\Omega_X\mathbf{H}_{X0}(t)$. Detailed calculations then show that [17]

$$S(\mathbf{q},\tau) = \left(\frac{e^2}{mc^2}\right)^2 \sin^2\phi \int_{-\infty}^{\infty} dt\, I_{0x}(t)\langle(\mathbf{q}, t+\tau) f(\mathbf{q}, t+\tau)\rangle \qquad (2)$$

where $S(\mathbf{q},\tau)$ is time-integrated intensity of the X-ray pulse, scattered τ seconds after optical excitation in the direction of the vector $\mathbf{q}_r - \mathbf{q}$. This expression can be deduced from that for $I_X(\mathbf{q})$ using the following arguments: (1) As the incident X-ray radiation is pulsed, one must replace I_{0X} by $I_{0X}(t)$. (2) Optical excitation brings the system out of thermal equilibrium. It no longer remains stationary but varies with time; thus $n(\mathbf{r}) \rightarrow n(\mathbf{r},t)$ and $f(\mathbf{q}) \rightarrow f(\mathbf{q},t) = \int d\mathbf{r}\exp(-i\mathbf{q}\mathbf{r})n$

$(\mathbf{r}, t)$. (3) The quantity $S(\mathbf{q}, \tau)$ is a time-integrated quantity. It is then useful to replace the integration variable t by the variable $t + \tau$, which permits one to introduce the time delay τ between the pump and the probe explicitly. (4) An X-ray diffraction experiment does not permit one to single out a given state of the system. Only an average $\langle\,\rangle$ over all these states can be observed.

C. Statistical Description of Optical Pumping

In the above Maxwellian description of X-ray diffraction, the electron number density $n(\mathbf{r}, t)$ was considered to be a known function of $\mathbf{r}$,t. In reality, this density is modulated by the laser excitation and is not known *a priori*. However, it can be determined using methods of statistical mechanics of nonlinear optical processes, similar to those used in time-resolved optical spectroscopy [4]. The laser-generated electric field can be expressed as $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_{\mathrm{O}0}(t)\exp(i(\mathbf{q}_{\mathrm{O}}r - \Omega_{\mathrm{O}}t))$, where Ω_{O} is the optical frequency and $\mathbf{q}_{\mathrm{O}}$ the corresponding wavevector. The calculation can be sketched as follows.

The main problem is to calculate $\langle f^*(\mathbf{q}, t+\tau) f(\mathbf{q}, t+\tau)\rangle$ of Eq. (2). To achieve this goal, one first considers $\mathbf{E}(\mathbf{r}, t)$ as a well defined, deterministic quantity. Its effect on the system may then be determined by treating the von Neumann equation for the density matrix $\rho(t)$ by perturbation theory; the laser perturbation is supposed to be sufficiently small to permit a perturbation expansion. Once $\rho(t)$ has been calculated, the quantity

$$\langle f^*(\mathbf{q}, t+\tau) f(\mathbf{q}, t+\tau)\rangle = \mathrm{Tr}[\rho(t+\tau) f^*(\mathbf{q}) f(\mathbf{q})] \tag{3}$$

can be determined for a given realization of the electric field $\mathbf{E}(\mathbf{r}, t)$. In the second step, this restriction to deterministic processes is suppressed and the incident laser field $\mathbf{E}(\mathbf{r}, t)$ is identified as a stochastic quantity. In reality, $\mathbf{E}(\mathbf{r}, t)$ is never completely coherent: averaging over this stochastic process is thus necessary. This can be done using theories of transmission of electric signals. The resulting expression is inserted into Eq. (2).

D. Difference Signal $\Delta S(\mathbf{q}, \tau)$

The theoretical difference signal $\Delta S(\mathbf{q}, \tau)$ is a convolution between the temporal profile of the X-ray pulse $I_{0\mathrm{X}}(t)$ and the diffraction signal $\Delta S_{\mathrm{inst}}(\mathbf{q}, t)$ from an infinitely short X-ray pulse. This expression is [17]

$$\begin{aligned}
\Delta S(\mathbf{q}, \tau) &= \int_{-\infty}^{\infty} dt\, I_{0\mathrm{X}}(t-\tau)\Delta S_{\mathrm{inst}}(\mathbf{q}, t) \\
\Delta S_{\mathrm{inst}}(\mathbf{q}, t) &= \left(\frac{e^2}{mc^2h}\right)^2 \sin^2\theta \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\tau_1\, d\tau_2 \\
&\quad \times \langle E_i(\mathbf{r}, t-\tau_1) E_j(\mathbf{r}, t-\tau_1-\tau_2)\rangle_{\mathrm{O}} \\
&\quad \times \langle [[f(\mathbf{q}, \tau_1+\tau_2) f^*(\mathbf{q}, \tau_1+\tau_2), M_i(\tau_2], M_j(0)]\rangle_{\mathrm{S}}
\end{aligned} \tag{4}$$

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