Ultrafast x-ray diffraction theory: time-scale considerations

Cao, Jianshu, Wilson, Kent

Jianshu Cao, Kent R. Wilson, "Ultrafast x-ray diffraction theory: time-scale considerations," Proc. SPIE 3273, Laser Techniques for Condensed-Phase and Biological Systems, (24 April 1998); doi: 10.1117/12.306131

Event: Optoelectronics and High-Power Lasers and Applications, 1998, San Jose, CA, United States

Ultrafast X-Ray Diffraction Theory: Time-scale Considerations

Jianshu Cao and Kent R. Wilson

Department of Chemistry and Biochemistry 0339, University of California, San Diego,
9500 Gilman Dr., La Jolla, CA 92093-0339

ABSTRACT

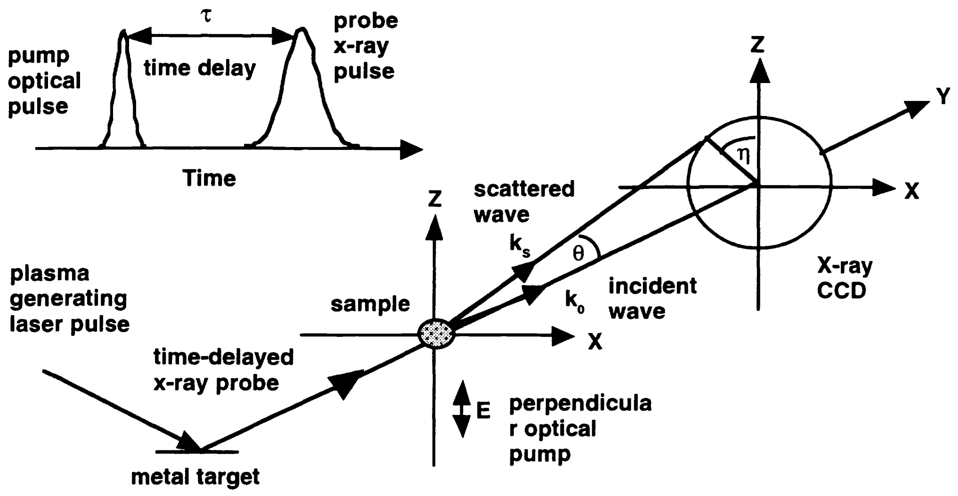
The dynamics induced in matter by a short optical pump pulse can be measured by time-resolved x-ray diffraction without resorting to additional and often unknown information (e.g., potential energy surfaces) as required in optical pump and probe experiments. Several theoretical aspects of such measurements are considered here: elastic versus inelastic scattering, quantum interference among electronic states, physical implications of temporal- and spatial-averaging, and the coherence of x-ray beams. Based on these considerations, it is possible to use inelastic scattering for studying curve crossing in molecular systems and electronic coherence in electronic materials, in addition to probing nuclear dynamics on an excited potential energy surface. With certain modifications, the time-dependent analysis presented here can be extended to other experimental methods including electron diffraction and x-ray absorption (chemical shifts, near-edge and EXAFS).

Keywords: ultrafast x-ray diffraction, laser-material interaction

1. INTRODUCTION

Ever since its discovery at the turn of the century,[1] x-ray diffraction has been employed to measure equilibrium molecular structures of a large number of molecules including polymers and proteins.[2] With the advance of ultrafast x-ray sources and detectors, time-resolved x-ray diffraction[3-6] can in principle provide dynamic pictures of electronic and nuclear motions during chemical and physical processes without resorting to any additional and unknown information often required in time-resolved optical experiments. In addition to diffraction, ultrafast extended x-ray absorption fine structure (EXAFS) and the near edge spectrum can be used to detect changes in local environments[7] and time-resolved chemical shifts of atomic absorption threshold can in principle be used to detect charge transfer or the oxidation state of chosen atoms. Thus, time-resolved x-ray diffraction and absorption techniques may soon emerge as powerful ways to observe the evolution of chemical reactions, the dynamics of biological systems, and the kinetics of structured materials.

Further author information –
Correspondance: Jianshu Cao; Email: jcao@chem.ucsd.edu;
For more information, please see our website, http://www-wilson.ucsd.edu.



The x-ray beam is generated by a thermal plasma on a metal surface illuminated by an ultrafast high intensity optical pulse, which is delayed by τ with respect to the pump pulse. In the perpendicular experimental arrangement, the polarization vector of the optical pump pulse (Z axis) is perpendicular to the incident wave vector of the x-ray probe pulse (Y axis). The incident x-ray photons propagating along the Y axis scatter at scattering angle θ with respect to the incident wave vector and at azimuthal angle η with respect to the polarization vector. The scattering vector s is the difference between the incident and scattered wave vectors.

As illustrated in the figure, in a time-resolved x-ray diffraction experiment, the dynamics of a sample is initiated by an ultrafast optical laser pulse and then probed by an ultrafast x-ray pulse at various delay times. As real-space configurations are inverted from x-ray diffraction patterns and are then recorded as a function of delay time, one can in principle follow the course of chemical and physical processes initiated by the optical pump pulse in real-time and real-space. To resolve the dynamics, the ultrafast x-ray experiment must have sub-picosecond temporal resolution for vibrational motions or bond making and breaking and sub-angstrom range spatial resolution for inter-nuclear distance.

The appealing prospect of real-time dynamics in real-space has motivated an increasing number theoretical and experimental studies of ultrafast x-ray diffraction and absorption.[3-9] However, the theoretical basis of time-resolved x-ray diffraction has not been fully elucidated, but is clearly required to interpret and invert x-ray data as the temporal resolution of x-ray detection approaches the limit of resolving electronic and nuclear dynamics. For this purpose, we examine several theoretical aspects related to time-scales in x-ray diffraction and then explore their implications in detecting real-time dynamics.[10]

2. THEORETICAL CONSIDERATIONS OF TIME-SCALES IN X-RAY DIFFRACTION

An optical pump pulse produces a non-stationary wave function, $\psi(t)$, which is then detected by an x-ray probe pulse, $E(t)$. The general starting point for x-ray diffraction theory is Born's perturbative theory for quantum scattering.[11] To first order in the scattering potential, the x-ray scattering operator is defined as

$$L(s) = \sum_{\mu} e^{isr_{\mu}} \tag{1}$$

where the summation μ extends to all electrons in the scattering center and the scattering vector s is the difference between the incident and the scattered wave vectors. Then, the scattering amplitude into a final state n can be expressed as

$$f_n(\vec{s}) = \int dt \langle \phi_n | e^{i\varepsilon_n t} L(\vec{s}) | \psi(t) \rangle E(t) \tag{2}$$

where irrelevant prefactors are ignored and ϕ_n is a final eigenstate wavefunction with eigen-energy ε_n. In time-independent x-ray diffraction theory, scattering intensity is simply the square of scattering amplitude. With time-resolved diffraction, the expression for scattering intensity is the result of several time-scale considerations, including coherence of x-ray sources and time-averaging, quantum interference among eigenstates, and elastic and inelastic scattering.[10]

2.1 X-ray coherence and temporal-averaging

For x-rays generated by a laser-driven plasma,[12] the x-ray beam consists of numerous spontaneous emission events such that an additional average over the photon statistics must be carried out on the intensity level. Under the assumption that the average coherence time of x-ray photons is significantly shorter than any dynamical time scale of the molecular system, we use a delta function to approximate the electric field self-correlation function

$$\langle E(t)E(t')\rangle_{ph} \approx A(t)\delta(t-t') \tag{3}$$

where $A(t)$ is the temporal envelope of the x-ray intensity. Then, the time averaging on the amplitude level in Eq. (2) is reduced to the time-averaging on the intensity level

$$I(\vec{s}) = \sum_n \int dt \langle \psi(t) | L^{+} | \phi_n \rangle \langle \phi_n | L | \psi(t) \rangle A(t) \tag{4}$$

where L^{+} is the complex conjugate of the scattering operator in Eq. (1). This expression can be easily recast into the density matrix representation if the molecular system is not a pure state.

2.2 Pulse duration and interference

As a result of the time-average of the scattering intensity over the x-ray pulse duration in Eq. (4), the coherence excited by the optical pump pulse is not detectable between any two eigenstates when their relative phase oscillates dramatically over the x-ray pulse. In other words, an incoherent x-ray pulse cannot detect quantum coherence on a time scale much shorter than the pulse duration. This is a consequence of the Heisenberg uncertainty principle: the shorter the x-ray pulse, the faster phase modulation it detects.

2.3 Elasticity and spatial-averaging

The range of the final state summation of Eq. (4) depends on the dynamic response of the x-ray diffraction measurement, which is the combined effect of the resolution of x-ray detection, the accessible energy of x-ray photons, or the finite pulse duration if the x-ray pulse is coherent. The physical meaning of the dynamic response becomes evident when it is related to the effective elasticity of a particular degree of freedom. To see this, we separate the coordinates into a set of slow coordinates, *R*, which appear frozen during x-ray scattering, and a set of fast coordinates, *r*, which appear delocalized during x-ray scattering. Then, invoking the completeness relation for the set of slow variables, we obtain the scattering intensity

$$I = \int dt \sum_n \left\langle \chi_n(t,R) \,|\, f_n(R) \,|^2\, \chi_n(t,R) \right\rangle_R A(t) \tag{5}$$

where $\chi_n(t,R)$ is a time-dependent wave function of the slow variables projected on n-th eigen-surface of the fast variables. Here, $f_n(R)$is the elastic scattering scattering amplitude on n-th eigen-state of the fast set of variables, defined as $f_n(R) = \left\langle \phi_n(r;R) \,|\, L \,|\, \phi_n(r;R) \right\rangle_r$ As indicated in Eq. (5), the slow variable set *R* is averaged on the intensity level and hence is inelastic, whereas the fast variable set *r is* averaged on the amplitude level and hence is elastic (at least partially).

3. EXAMPLES OF ULTRAFAST X-RAY DIFFRACTION

3.1 X-ray measurement of electronic dynamics in atomic systems

Application of ultrafast diffraction to atomic systems and molecular systems with frozen atoms is relatively simple because the nuclear degrees of freedom are not included in the analysis. For inelastic scattering with short x-ray pulses, the scattering intensity is given as

$$I(s) = \int dt A(t)[N + \int dr \rho_2(t,r) e^{isr}] \tag{6}$$

where *N* is the number of electrons and $\rho_2(t,r)$ is the time-dependent two-body electron correlation function defined as

$$\rho_2(t,r) = \sum_{\mu \neq \nu} \left\langle \psi(t) \,|\, \delta(r - r_\mu + r_\nu) \,|\, \psi(t) \right\rangle \tag{7}$$

with electron indices μ and ν. As implied in the above discussion, sub-femtosecond x-ray pulse durations are required to resolve electronic coherence among widely separated electronic states. This is no longer true when electronic states are sufficiently close, as in large molecules and Rydberg states.[13] The expression for $\rho_2(t,r)$ can be easily recast into a density matrix representation if electronic dephasing is present.

The spatial dependence in $\rho_2(t,r)$ describes electronic correlation and the temporal dependence in $\rho_2(t,r)$ describes electronic coherence. In fact, $\rho_2(t,r)$ can be understood as a reduced two-dimensional description of electronic structure and dynamics. As has been demonstrated, such a reduced description relates electronic structures to optical properties and hence provides a unified framework for studying electronic structures and dynamics in conjugated polymers, semiconductors, nanostructures and biological complexes.[14] For this purpose, x-ray diffraction is a direct measurement of time-dependent two-body electron distribution functions.

3.2 Solving molecular dynamics from x-ray diffraction

The general time-scale analysis can be applied to molecular systems with the help of the Born-Oppenheimer separation of electronic, vibrational, and rotational degrees of freedom. Depending on temporal or energy resolution, one can treat electronic (femtoseconds), vibrational (picoseconds), and rotational (nanoseconds) degrees of freedom as elastic, mixed, or inelastic scattering variables. For sub-picosecond x-ray diffraction, it is reasonable to treat electrons as elastic and nuclei as inelastic, which agrees well with the separation of electronic and nuclear degrees of freedom in the Born-Oppenheimer approximation. Then, in Eq. (5), $\chi_n(t,R)$ is the non-stationary ro-vibrational wave function evolving on the n-th electronic surface and $f_n(R)$ is the elastic electronic scattering amplitude on the n-th electronic surface. To simplify the analysis, we invoke the independent atom model (IAM),[11] which assumes that atoms are well-localized and hence scatter x-ray photons independently. This is a reasonable assumption because the scattering comes mainly from core electrons which are not sensitive to nuclear dynamics. With the Born-Oppenheimer approximation and the independent atom model, molecular dynamics can be directly probed without references to electronic density, which is the working principle for all current ultrafast x-ray experiments.

If some electronic states are too close to be resolved by x-ray detection, as in the case of curve crossing or high-lying electronic states, the relevant electronic degrees of freedom cannot be treated as completely elastic. Then, the general expression as discussed in the last section is required to describe the electronic coherence in additional to nuclear dynamics. In the simplest case of two coupled electronic surfaces, a femtosecond x-ray pulse can reveal quantum beats in the crossover regime and the oscillation of the beats is modulated by nuclear motions. Thus, ultrafast x-ray diffraction can be a useful way to study nonadiabatic dynamics in molecular systems.

4. CONCLUDING REMARKS

In this paper, we have investigated several theoretical aspects of time-scales involved in ultrafast x-ray diffraction, which are necessary to extend stationary x-ray theory to time-dependent x-ray theory. It is evident that the analysis of a particular ultrafast x-ray diffraction experiment has to take into account these time scale considerations.[10] Though presented in the context of ultrafast x-ray diffraction, these theoretical treatments, especially the time scale considerations, can also be used to analyze other time-resolved experimental methods.

5. REFERENCES

1. W. C. Roentegn, "On a new kind of ray", *Nature* **53**, 274, 1896
2. J. D. Watson and F. H. C. Crick, "A structure for deoxyribose nucleic acid", *Nature* **171**, 737 1953
3. P. M. Rentzepis, Time-resolved Electron and X-ray Diffraction, *Proc. SPIE* **2521**, 1995.
4. R. W. Schoenlein, W. P. Leemans, A. H. Chin, P. Volfbeyn, T. E. Glover, T. E. Balling, M. Zolotorev, K. J. Kim, S. Chattopadhyay, and C. V. Shank, "Femtosecond x-ray pulses at 0.4 A generated by 90° Thomson scattering: A tool for probing the structural dynamics of materials", *Science* **274**, 236, 1996.
5. T. Guo, C. Rose-Petruck, R. Jimnez, F. Ráksi, J.Squier, B. Walker, K. R. Wilson, and C. P. J. Barty, "Applications of x-rays generated from lasers and other bright sources", eds. G.A. Kyrala and J-C. Gauthier, *Proc. SPIE* - **3157**, 84, 1997
6. C. Rischel, A. Rousse, I. Uschmann, O. A. Albouy, J. P. Greindre, P. Audebert, J. C. Gauthier, E. Fordter, J. L. Martin, and A. Antonetti, "Femtosecond time-resolved x-ray diffraction on laser-heated organic films", *Nature* **390**, 490 (1997).
7. F. Ráksi, K. R. Wilson, Z. Jiang, A. Ikhlef, C. Y. Cote, and J. C. Kieffer, "Ultrafast x-ray absorption probing of a chemical reaction", *J. Chem. Phys.* **104**, 6066 (1996).
8. S. H. Lin, C. H. Chao, H. Ma, and P. M. Rentzepis, in Time-Resolved Electron and X-ray Diffraction, edited by P. M. Rentzepis, *Proc. SPIE* **2521**, p258, 1995.
9. M. Ben-Nun, J. Cao, and K. R. Wilson, "Ultrafast x-ray and electron diffraction: Theoretical considerations", *J. Phys. Chem.* **101**, 8743, 1997
10. J. Cao and K. R. Wilson, "Ultrafast x-ray diffraction theory", *J. Phys. Chem.* 1998, in preparation.
11. B. K. Agarwal, X-ray Spectroscopy: An Introduction, Springer-Verlag, Berlin, 1991.
12. M. M. Murnane, H. C. Kapteyn, and R. W. Falcone, "Ultrafast x-ray pulses from laser-produced plasma", *Phys. Rev. Lett.* **62**, 155, 1989.
13. J. L. Krause, K. J. Schafer, M. Ben-Nun, and K. R. Wilson, "Creating and detecting shaped Rydberg wave packets", *Phys. Rev. Lett.*, 1998, in press.
14. S. Mukamel, S. Tretiak, T. Wagersreiter, and V. Chernyak, "Electronic coherence and collective optical excitations of conjugated molecules", *Science* **277,** 781, 1997.