Perspective: characterizing coherences in chemical dynamics with attosecond time-resolved x-ray absorption spectroscopy

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Coherence can drive wave-like motion of electrons and nuclei in photoexcited systems, which can yield fast and efficient ways to exert materials' functionalities beyond the thermodynamic limit. The search for coherent phenomena has been a central topic in chemical physics, although their direct characterization is often elusive. Here, we highlight recent advances in time-resolved x-ray absorption spectroscopy (tr-XAS) to investigate coherent phenomena, especially those that utilize the eminent light source of isolated attosecond pulses. The unparalleled time and state sensitivities of tr-XAS in tandem with the unique element specificity render the method suitable to study valence electronic dynamics in wide variety of materials. The latest studies have demonstrated the capabilities of tr-XAS to characterize coupled electronic-structural coherence in small molecules, as well as coherent light-matter interactions of core-excited excitons in solids. We address current opportunities and challenges in the exploration of coherent phenomena, with potential applications for energy- and bio-related systems, potential crossings, strongly driven solids, and quantum materials. With the ongoing developments in both theory and light sources, tr-XAS holds great promise for revealing the role of coherences in chemical dynamics.

I. INTRODUCTION

One of the hallmarks of quantum mechanics is coherent phenomena, which arise from interference of multiple wavefunctions with fixed phase differences. An overview of coherent phenomena that can play roles in photoexcited materials is shown in Fig. 1. These examples include prompt dissociation of chemical bonds on excited potentials,[1] recurrence of bound-state wavefunctions that correspond to molecular vibrations and rotations,[2,3] and wave-like propagation of electron density in molecular complexes.[4] Coherence can enable prompt completion of chemical reactions or efficient energy transfer beyond the thermodynamic limits, and its possible implications in energy- and bio-related materials have been attracting wide interest.[5]

Recent advances in ultrafast spectroscopy, particularly the methodology to generate isolated attosecond pulses in the extreme-ultraviolet (XUV) to soft x-ray regimes,[6] have turned the attention of physical chemistry toward increasingly short and fundamental processes in chemical dynamics.[7] Coherent electronic motions that occur in photoexcited molecules before the onset of nuclear motions, which could ultimately determine the fate of photochemical reactions, are one such phenomenon that has become accessible by attosecond spectroscopy.[8] In this Perspective, we overview the latest progress on the search for coherent phenomena by means of attosecond spectroscopy. The emphasis is placed on those phenomena that involve electronic coherence, which, for the case of valence orbitals, occur on a few- to sub-femtosecond time scale.

Among the several spectroscopic applications of attosecond pulses, we focus on time-resolved x-ray absorption spectroscopy (tr-XAS).[9] Tr-XAS is a pump-probe technique in which a strong excitation by an ultraviolet or visible optical pulse triggers a photochemical reaction, and a subsequent attosecond XUV/x-ray pulse encodes the dynamics in its transmission spectrum. The probing step relies on core-to-valence transitions, wherein element specificity is achieved by the localized nature of core orbitals, while transitions to unoccupied valence orbitals enable sensitive probing of the surrounding chemical environment. As we will overview, many other categories of photoexcited dynamics, those that were beyond the temporal and spectral resolution of the other spectroscopic techniques, have been characterized with tr-XAS.

The objective of this article is to provide a brief overview and future perspectives on the intersection of the two emerging areas, coherent chemical dynamics and tr-XAS. For readers interested in broader perspectives of these individual topics, we refer them to Krausz *et al.* for general overview of attosecond science,[10] and Kraus *et al.* for ultrafast x-ray experiments on chemical dynamics.[11]

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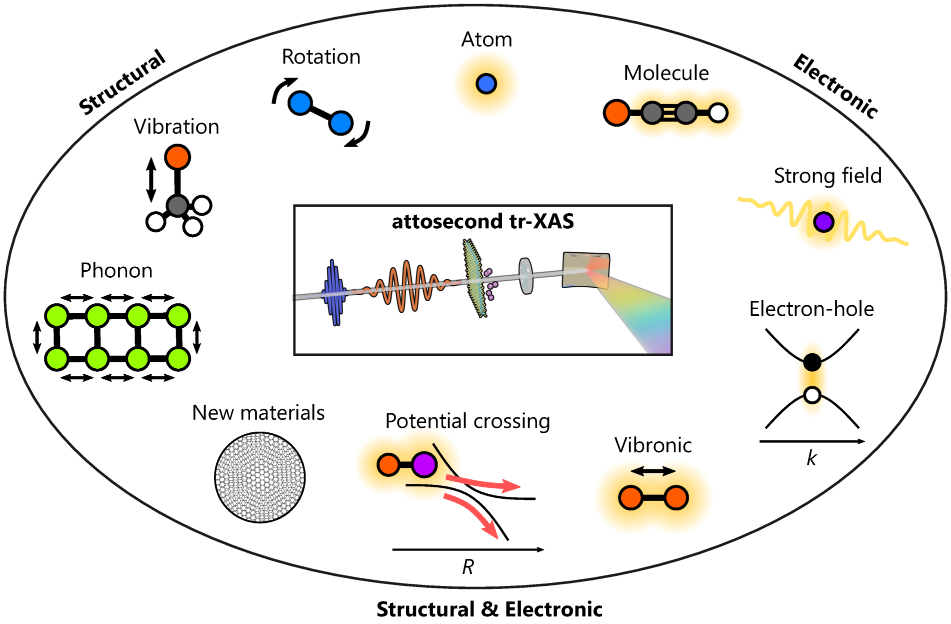

FIG. 1. **Overview of coherent phenomena in chemical physics via tr-XAS.** Examples of coherent structural dynamics include molecular vibration, rotation, and solid-state phonon. Electronic coherence can be induced in atoms, molecules, during strong light-matter interactions, and between electrons and holes in solids. Coupled interplay of electronic-structural coherence will play a role in potential crossings and vibronic superpositions.

For the specific topic of charge migration, Wörner *et al.* provides an excellent review on this central issue of attosecond science.[12] For coherences related to functionalities of chemical and biophysical systems, Scholes *et al.* summarizes some of the latest results.[5] Chemical applications of tr-XAS have been first pioneered in large-scale facilities such as synchrotrons and free-electron lasers; see Chergui and Collet for a comprehensive review.[13] Lastly, coherence has long been investigated in a broad context from atomic physics to quantum computing; see Alber and Zoller for an early review on Rydberg wavepackets.[14]

II. RECENT EXPERIMENTAL PROGRESS

A. How tr-XAS can probe coherences

The basic concept of how tr-XAS can resolve coherences in photoexcited systems is shown in Fig. 2. Coherent structural dynamics, such as molecular vibration or bond dissociation, can be described by a coherent superposition of structural eigenstates [Fig. 2(a)]. The time evolution of such a superposition leads to coherent motion of a nuclear wavepacket along a reaction coordinate, which can be probed as time-dependent shifts of the absorption signals in the x-ray spectra. The direction of the peak shift contains information on the bonding/antibonding nature of the unoccupied valence orbitals.[15] Coherent electronic dynamics can be induced when a system is established in a coherent superposition of multiple electronic states. In the case of pure electronic coherences, i.e., when there are no structural dynamics involved, as is always the case for atomic systems, an electronic superposition can be probed as a periodic modulation of absorption amplitude with nominally fixed frequency. In practice, electronic dynamics in molecules usually are accompanied by structural dynamics that occur on a slower time scale. The time evolution of transient-absorption signals is given by a combination of peak shifts and amplitude modulation, with possible seemingly varying frequencies due to the main rovibronic spectroscopic contributions to the modulation features.

B. Coherent structural dynamics

The capability of tr-XAS to resolve coherent structural dynamics of molecules was highlighted initially in an experimental work on bromine molecules (Br_2).[17] In the experiments, strong-field ionization launched vibrational wavepackets in the neutral and ionic states of bromine, and XUV absorption at the Br-3d edge characterized their time evolution as a function of the internuclear separation of the wave packet. Importantly, it was shown that the steep potential of the core level versus internuclear separation provides a large time-resolved shift in the XUV absorption spectrum. The phase information of the vibrational motions that is directly made available by the real-time tracking provides valuable insights into the preparation mechanism of the vibrational wavepackets, and the degree of shift characterizes the steepness of the core level potential. Theoretical mod-

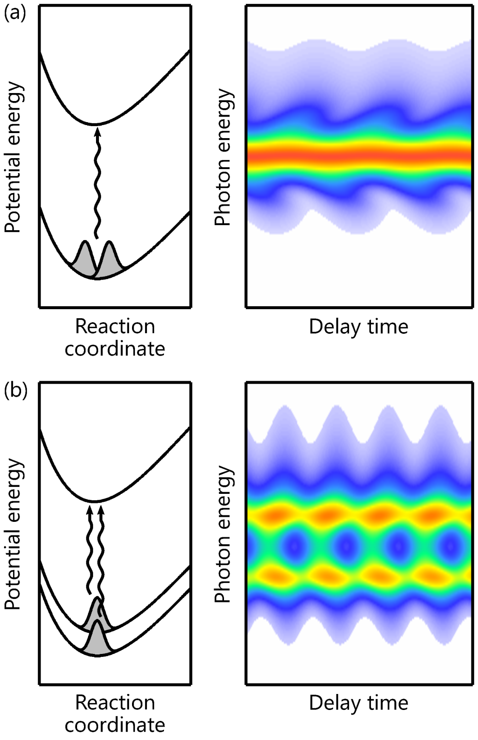

FIG. 2. **Probing mechanisms of coherences in tr-XAS.** (a) Vibrational coherences induce coherent structural dynamics in chemical systems, which translates to delay-dependent variations in the x-ray absorption energies. (b) A coherent superposition of electronic states will lead to characteristic modulation in the absorption amplitude, or quantum beats. Adapted with permission from Kobayashi *et al.,* Phys. Rev. A **101,** 063414 (2020).[16] Copyright (2020) by the American Physical Society.

eling of the transient-absorption spectra on vibrational wavepackets was reported for fluorine molecules (F_2).[18] The work showed the route to calculate core-excited potentials of halogen molecules, further revealing accurate bond-length dependences of the core-to-valence absorption signals. In the following years, molecular vibrations have been characterized for a variety of systems such as I_2,[19] N_2O,[20] and C_2H_3Br.[21] Multimode motions have been resolved in alkyl iodides, showing the applicability of the method to polyatomic systems.[22–24] These aspects are further explored in polyatomic molecules of SF_6, where both the minimum detectable shift and the slope of the core level potentials are accurately defined.[25,26]

Rotational motion of molecules has also been characterized by tr-XAS. A series of recent experiments with tr-XAS reported characterization of rotational wavepackets in nitrogen (N_2), oxygen (O_2), and hydrogen (H_2).[27,28] The results enabled experimental assignments of the symmetry to molecular Rydberg states. It is also shown that the dynamic variation in the absorption lineshape induced by rotational coherence can lead to optical gain of the XUV light. Manifestation of rotational motion in the x-ray absorption spectra can be relatively subtle compared to vibrational motions since the probing mechanism depends on the anisotropic angular distribution of the valence unoccupied orbitals. Nevertheless, the experiments showed that tr-XAS can probe such anisotropy in small molecules and reconstruct the time evolution of the rotational wavepacket.[27,28]

Structural sensitivity of tr-XAS has also been demonstrated for solid materials. Compared to vibrational motions in gas-phase molecules, which can cause atomic displacements on the order of $> 10\%$,[29] photon dynamics in solids induce smaller distortions, typically less than a few percent. Despite that, an early experimental work that employed time-resolved x-ray reflectivity spectroscopy successfully characterized the A_{1g} mode of an optical-phonon motion in bismuth.[30] Since then, coherent phonon dynamics have been characterized for several other solid systems such as $LiBH_4$,[31] $MoTe_2$,[32] and bismuth.[33] Tr-XAS is known as a powerful technique to probe electron and hole dynamics in solids.[34] These results show the versatility of the method to study photoinduced processes in condensed-matter systems, including the structural dynamics and coherences therein.

C. Coherent electronic dynamics

The first successful characterization of coherent electronic dynamics with tr-XAS was reported in atoms.[35] In the experiment, strong-field ionization by a near-infrared pulse launched a coherent superposition of the spin-orbit doublet states in krypton ions. Valence-electron motion driven by electronic coherence, which corresponds to oscillation of hole density along the direction of ionization, was characterized as 6.3-fs quantum beats in the attosecond-absorption signals. The signal discrimination is obtained through the polarization direction of the pump and probe light. The experimental results were directly compared to theoretical models, and the degree of electronic coherence was determined to be $g = 0.6$. The same experimental concept has been applied to coherent electronic dynamics in the double ionization of xenon[36] and strong-field ionization of polyatomic systems.[37] These studies have shown remarkable features of tr-XAS, including subfemtosecond temporal resolution, spin-orbit state resolution, and the ability to quantitatively characterize the degree of coherence when combined with theoretical calculations. Furthermore, a recent experimental study on deuterium bromide ions (DBr^+) characterized electronic and vibrational coherences simultaneously (Fig. 3a), showing the powerful capability of the method to capture multidomain coherences.[16]

Several studies have reported the characterization of coherent electronic dynamics during light-matter interactions. For example, tr-XAS was used to investigate subcycle dynamics of strong-field ionization in xenon atoms.[38] The transient-absorption spectra characterized half-cycle buildup and overshoots in the ionic signals,

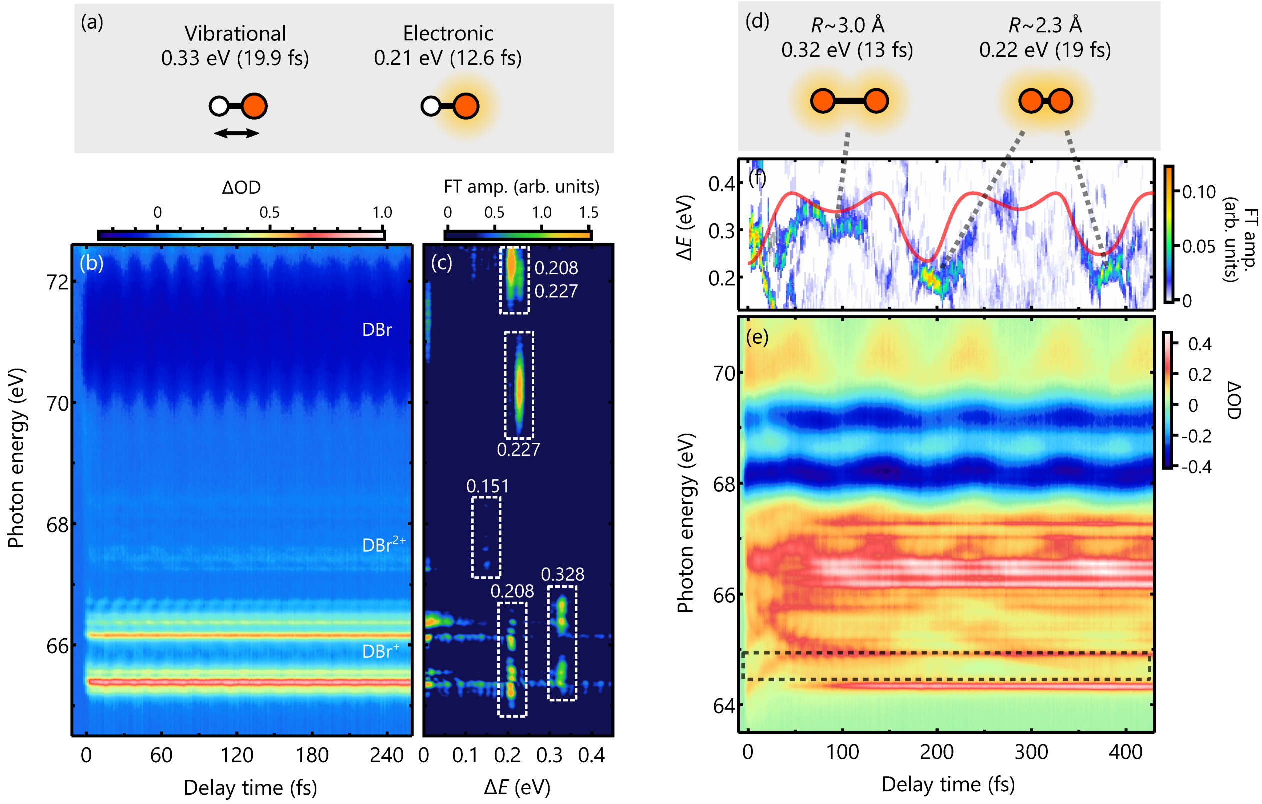

FIG. 3. **Electronic-vibrational coherences characterized by attosecond tr-XAS.** (a-c) Electronic and vibrational coherences characterized for DBr$^+$. The quantum beats in the DBr$^+$ signals show two characteristic frequencies at 0.208 eV and 0.328 eV, which correspond to vibrational and electronic coherences, respectively, in the $X\ ^2\Pi_{3/2,1/2}$ states, respectively. Adapted with permission from Kobayashi *et al.,* Phys. Rev. A **101,** 063414 (2020).[16] Copyright (2020) by the American Physical Society. (d-f) Vibronic quantum superpositions characterized by attosecond tr-XAS in Br$_2^+$. The window Fourier-transformation results (f) reveal apparent decay, revival, and apparent frequency shift in the electronic quantum beats. Adapted with permission from Kobayashi *et al.,* Phys. Rev. A **102,** 051102 (2020).[29] Copyright (2020) by the American Physical Society.

revealing reversible (coherent) and irreversible (incoherent) processes of strong-field ionization. A recent experimental work characterized subcycle ionization dynamics in nitric oxide (NO) by using attosecond soft-x-ray pulses to access the nitrogen K-edge at $\sim$ 400 eV.[20] This study also measured molecular vibration and rotation that occur after the ionization, highlighting the versatility of tr-XAS. In the experiments on solid systems, tr-XAS was used to probe the subcycle response of the dynamic Franz-Keldysh effect (i.e., renormalization of band structure by an intense laser field) induced by a strong near-infrared pulse.[39] The probed dynamics correspond to subcycle motion of the intraband transition induced by an intense, subbandgap excitation. Attosecond x-ray pulses can also be used to access core-level excitons, i.e., quasiparticle bound states formed by an electron-hole pair based on the removal of an electron from the core orbital of an atom. Subcycle dynamics of the light-dressing effects to core-level excitons were investigated in MgO[40] and MgF$_2$[41] with time-resolved x-ray reflectivity measurements. These studies also present direct measurements of the intrinsic lifetimes of the short-lived states in solids.

III. FUTURE OPPORTUNITIES CHALLENGES

A. Charge migration

One of the prominent phenomena induced by electronic coherence is charge migration. This phenomenon is realized when a coherent superposition of valence electronic states is created among the wavefunctions that are delocalized throughout the molecular structure and have spatial overlap with each other. Experimentally, photoion spectroscopy and high-harmonic spectroscopy have been used to probe these dynamics following photoionization of gas-phase molecules.[42,43] Tr-XAS is calculated to achieve a panoramic reconstruction of charge migration by simultaneously accessing two or more tagging elements with a broadband x-ray spectrum.[44] The spatial information of charge migration is imprinted in complex transition dipole phases of core orbitals, which translates to relative timings of quantum beats in different element windows.[45] Tr-XAS can resolve subsequent structural dynamics, which include the interplay between the electronic and structural degrees of freedom, thus enabling us to obtain a complete picture of the photoexcited molecular dynamics.

B. Vibronic coherence

Coherent electronic dynamics in molecules can entail slower nuclear motions such as bond dissociation or vibrations. In these cases, energy can be exchanged between the electronic and nuclear degrees of freedom, or energy landscapes of electrons can be altered adiabatically or nonadiabatically as the molecular structure changes. Such electronic-nuclear couplings can damp electronic coherence through dephasing (reversible) or decoherence (irreversible). Experimentally, apparent frequency shifts of electronic quantum beats can be caused by nuclear motions. Tr-XAS has been recently shown to be capable of probing such electronic-nuclear dynamics in a diatomic system of bromine ion (Br_2^+) (Fig. 3b).[29] In the experiments, instantaneous frequencies of the quantum beats are shown to change between 0.22 eV and 0.32 eV in synchrony with the molecular vibration. This is because the detection energies of the electronic quantum beats are changing as the molecule undergoes coherent vibrational motion (combined electronic-vibrational transitions). These results provide the first experimental observation of decay, revival, and apparent frequency shifts of electronic coherence caused by concurrent vibrational motions, which was only predicted in theory.[46,47] It is further predicted that by extending the measurements to a picosecond range one can obtain the molecular vibronic structure imprinted as discrete progressions in electronic-beat frequencies. We envision that more experimental studies will follow with a focus on vibronic coherence between delocalized valence orbitals in polyatomic systems, which can lead to charge migration. A recent attosecond tr-XAS study reported long-lived radial charge migration in silane (SiH_4) and decoherence and revival therein.[48] It is also notable that attosecond four-wave mixing, which can access XUV-excited Rydberg states in molecules, has been applied to characterize vibronic quantum superpositions in hydrogen molecules (H_2).[49]

C. Potential crossings

Potential crossings, such as conical intersections and avoided crossings, play an ubiquitous role in photochemistry by serving as a funnel to transfer population between neighboring states.[50,51] Theoretical studies predict that a coherent superposition of electronic states can be created when a photoexcited molecule meets a potential crossing and bifurcates into two reaction pathways.[52,53] Moreover, theory predicts that molecular dynamics at potential crossings can be steered by tuning the phase of electronic coherence, which will open a path toward the concept of attochemistry.[54,55] Tr-XAS has been shown to be able to characterize potential crossings by mapping the abrupt switching of electronic character in the core-to-valence absorption signals from gas-phase molecules.[56–59] Electronic coherence at potential crossings can further be revealed by tr-XAS as characteristic quantum beats in the absorption spectra. Careful choice of the target molecule that can exhibit strong coherence as well as selective excitation to the desired electronic states will be indispensable, both of which will be highly benefitted by theoretical calculations. It is also notable that novel probing schemes beyond tr-XAS have been proposed, such as transient redistribution of ultrafast electronic coherences in attosecond Raman signals (TRUECARS).[52] This method is advantageous over tr-XAS in that it is only sensitive to coherent components of the system and thus is capable of providing background-free measurements.

D. Coherent control

Controlling coupled dynamics of electrons and nuclei in multiphoton or strong-field photoexcited molecules is possible with pulse-shaping techniques.[60,61] One of the common experimental schemes is to measure product fragments with photoion spectroscopy while applying closed-loop feedback to optimize the pulse shapes for desired outcomes. There remains a gap, however, in our understanding of the molecular response during and after the excitation with shaped laser pulses. Tr-XAS has a potential to fill this gap by directly accessing coherent electronic-nuclear dynamics in molecules with subfemtosecond time resolution. A limitation along this line is that tr-XAS is not suited to study minor reaction pathways, and thus the dynamics of interest need to be a significant fraction of the total yield. Decoding the elusive processes of subcycle electronic motions in a molecule, electronic excitation pathways, and ensuing structural dynamics is central to the ensuing chemical dynamics.

E. Biophysical systems

Spectroscopic experiments on the solution-phase Fenna-Matthews-Olson bacteriochlorophyll complex have shown there are long-lived coherences in these photosynthetic systems after excitation by a femtosecond laser pulse.[62] The results suggested the possibility of natural systems harnessing electronic coherence for efficient energy transfer in photosynthesis. Meanwhile, the origin of the long-lived coherences has been a topic of vigorous debate as the observed beat frequencies approximately match those of the vibrational motions.[63–68] Tr-XAS can probe both vibrational and electronic coherences by projecting them differently in transient absorption spectra (Fig. 2); electronic coherence will cause amplitude oscillation in the tr-XAS spectra, while vibrational coherence will lead to a periodic peak shift. The element specificity of core-level absorption can be effectively utilized for large chemical complexes with multiple reporter atoms, which enables direct reconstruction of the delocalized coherent electronic dynamics. It is challenging to apply x-ray pulses to the photosynthetic complexes as these molecules are usually prepared in a solvent. Once realized, however, new insights into the origin of the long-lived coherences might be obtained.

F. Coherence in solvents

Extending the probing photon energy into the so-called water-window regime (> 300 eV) will enable tr-XAS experiments in the liquid phase.[69–72] Photochemical reactions in a liquid consist of a number of steps where coherence can play a role; photoexcitation, electron transfer, structural rearrangement, and relaxation of solvation shells.[73] For example, a recent x-ray scattering experiment has revealed coherent translational motions of a solvation shell in a charge-transfer process of a metal complex in water, showing that solvent coherences can occur upon ultrafast photoexcitation.[74] It is an intriguing question whether tr-XAS can resolve such solvation-shell dynamics in a liquid on top of the initial charge-transfer or charge-migration process. The element specificity of the method can separate the dynamics occurring in the solute shell and solvent molecules. Combining an attosecond beamline with a vacuum liquid-microjet setup is extremely challenging, but an experimental implementation of such design has been reported for attosecond photoemission experiments.[75] Development of a liquid flatjet that has a few microns of thickness is also critical to carry out tr-XAS in the transmission geometry,[76] which allows for deciphering solvent dynamics in the bulk.

G. Strongly driven electrons and holes

Electronic coherence plays a crucial role in light-induced processes in solid-state materials. One of the examples is solid-state high-harmonic generation, wherein strongly driven electrons and holes trigger subcycle emission of high-energy photons.[77–79] One of the mechanisms of solid-state high-harmonic generation is interband polarization, which is given by the time evolution of coherent electron-hole pairs formed by laser excitation.[80] Lifetimes of electron-hole coherence in semiconductors have been measured to be > 10 fs under perturbative excitation.[81] However, in the simulations of high-harmonic generation, extremely short coherence lifetimes on the order of a few femtoseconds are employed phenomenologically.[82] Experimental measurement of such short lifetimes of strongly driven electron-hole pairs has yet to be done. Tr-XAS has the potential to achieve direct characterization of the electron-hole lifetimes with its superb temporal resolution. Strong-field driving of solids is an active area of research bridging materials science and ultrafast spectroscopy.[83] Successful application of tr-XAS to unravel the mechanisms of solid-state high-harmonic generation will have a broad impact, shedding light on better design of compact and efficient attosecond x-ray light sources.[84]

H. Two-dimensional materials

Monolayer transition-metal dichalcogenides (TMDs) have recently been attracting wide attention in science as a new platform for optoelectronic devices.[85] Bulk TMDs are layered crystals just like graphite, and one can isolate their monolayers by using the scotch-tape exfoliation technique. TMDs are gapped materials unlike graphene and they can host strong excitons, i.e., quasiparticle bound states resulting from electron-hole interactions.[86] Layer stacking of TMDs enables one to design new electrical, optical, and magnetic properties of the excitons.[87] As shown by recent experiments on bulk TMDs,[32,88] attosecond XUV pulses can access multiple element edges of TMDs. The element specificity and wide spectral coverage of tr-XAS open particularly intriguing opportunities for heterostructure samples. For example, formation of interlayer excitons and charge migration across the atomic layers can be directly visualized. Within monolayers, coherence can be formed between different excitonic states by a broadband visible excitation and the coherent charge-density modulation can be characterized by attosecond tr-XAS. Experimentally, monolayer materials will present an outstanding challenge in obtaining absorption signals above the detection threshold. Stable light sources combined with noise-reduction techniques such as heterodyne detection will be indispensable.

I. Entangled states

Entanglement is a concept in quantum mechanics that describes the correlation between two domains (e.g. photoelectrons and photoions).[89–91] Entanglement can affect how coherences manifest themselves in experimental observables, but little has been studied for the potential role of entanglement in attosecond science. A series of recent studies investigated the effect of entanglement in an attosecond pump-probe experiment on hydrogen molecules in the gas phase (H_2).[92,93] In the experiments, a pair of XUV pulses photoionize hydrogen molecules to launch an ion plus photoelectron wavefunction. The ion-photoelectron entanglement can hinder the interference of vibrational wavefunctions in the ionic states when the entangled photoelectrons have distinguishable kinetic energies. The measurements show that the vibrational coherence exhibits suppression and enhancement as a function of the XUV-XUV delay, which is identified as a signature of the ion-photoelectron entanglement. Entanglement can be considered in other systems, for example, between electronic and vibrational degrees of freedom in photoexcited molecules. In a series of theoretical studies on cesium molecules (Cs_2),[90,94] it was predicted that the electronic-vibrational entanglement can be deduced by measuring the electronic coherence. Tr-XAS is a powerful technique to characterize electronic coherences and its capabilities have already been demonstrated for small molecules.[16] Application of tr-XAS to entanglement problems also awaits progress in theory[95]. It will require a theoretical framework to associate experimentally measurable quantum beats in absorption signals to the underlying coherence and entanglement. Entanglement is an emerging topic in attosecond science, and we expect more studies to follow in the near future.

IV. SUMMARY

The new light source of attosecond x-ray pulses has been established as a powerful tool to study chemical dynamics. In particular, time-resolved x-ray absorption spectroscopy (tr-XAS) has been successfully applied to characterize coherent phenomena in photoexcited atoms, molecules, and solids. The early experimental studies have already discovered new phenomena that occur on unprecedented time scales, such as valence electronic coherence launched by strong-field ionization[35] and subcycle ionization dynamics in atoms and solids.[38,96] Transient absorption is based on a fully coherent process of dipole transitions, and this enables direct and quantitative evaluation of electronic coherences in targeted systems.[97] Core-to-valence absorption is also sensitive to subtle changes in the chemical environment that are sensed by the valence unoccupied orbitals.[15] Therefore, the structural dynamics as well as the coupled interplay between the electronic and structural degrees of freedom can be characterized. The element specificity and the subfemtosecond temporal resolution of the attosecond x-ray/XUV pulses are central to the capability of the method to reconstruct valence-electronic motions in real time.

First-principles calculations will continue to play a crucial role in the tr-XAS studies. There is an uncertainty whether coherence, be it electronic or structural, can be prepared in large chemical systems with high enough amplitude and long enough lifetime to be detected in experiments.[7] There is also a significant chance that the competing vibrational motions will promptly suppress the coherent electronic motion. Theoretical prediction of robust coherence is indispensable to design an experiment, and latest studies have demonstrated such predictions for several polyatomic systems.[98,99] Interpretation of transient-absorption signals becomes a nontrivial task when the pump and probe pulses are overlapping in time. To characterize strongly driven dynamics such as strong-field ionization and high-harmonic generation, theory will be required to disentangle the underlying coherences and the lineshape modulations.[100,101]

Developments in attosecond light sources and instruments have been remarkable over the last several years. Attosecond soft x-ray pulses have been generated and used for spectroscopy reaching > 400 eV,[20,102,103] which enables one to access K and L edges of some of the elements in the 2nd and 3rd element periods, respectively. New x-ray optics have been devised such as gas-phase refractive lenses,[104] plasma-based atto-chirp compensation,[105] and XUV-phase retarders that enable one to create circularly polarized attosecond pulses for circular-dichroism experiments.[106] In addition to the attosecond probe, it is equally important to establish an intense and ultrafast pump that allows for selective excitation of the targeted coherences. Most of the studies so far have used strong-field ionization by a few-cycle near-infrared pulse as a pump, while few-femtosecond ultraviolet-visible light can resonantly access neutral excited states that are more relevant to photochemical reactions in nature.[24,107,108] It is also notable that there are other techniques with attosecond x-ray pulses that have been proposed or already applied in coherent experiments. Attosecond four-wave mixing has been successfully applied to probe vibronic quantum superpositions in hydrogen molecules (H_2),[49] and the method was recently extended to probe few-femtosecond core-exciton dynamics in a solid material of sodium chloride (NaCl).[109] Other examples include circular dichroism,[106] and transient redistribution of ultrafast electronic coherences in attosecond Raman signals (TRUECARS).[52]

As we highlighted, there are numerous opportunities and challenges about coherent dynamics that can be addressed with tr-XAS. The quantum nature is ubiquitous in molecules, condensed matter, and even in light.[110] With the recent demonstration of characterizing electronic and structural coherences in small systems, as well as the rapid progress in the theoretical tools to study coherent phenomena, we are at an exciting moment for coherent chemical dynamics and their spectroscopic studies.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yuki Kobayashi: writing (major). **Stephen R. Leone:** writing (perspective); supervision (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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