ATTOSECOND PHYSICS

Soft x-ray excitons

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The dynamic response of excitons in solids is central to modern condensed-phase physics, material sciences, and photonic technologies. However, study and control have hitherto been limited to photon energies lower than the fundamental band gap. Here we report application of attosecond soft x-ray and attosecond optical pulses to study the dynamics of core-excitons at the L$_{2,3}$ edge of Si in silicon dioxide (SiO$_2$). This attosecond x-ray absorption near-edge spectroscopy (AXANES) technique enables direct probing of the excitons’ quasiparticle character, tracking of their subfemtosecond relaxation, the measurement of excitonic polarizability, and observation of dark core-excitonic states. Direct measurement and control of core-excitons in solids lay the foundation of x-ray excitons.

In semiconductors, dielectrics, macromolecules, and clusters, electrons and holes form fundamental, hydrogen-like quasiparticles (excitons) that underlie a broad range of applications in photonics and electronics (1). Coherent ultrafast nonlinear spectroscopies (2) in the terahertz, infrared, and optical ranges (3) can now directly identify quasiparticles formed below the fundamental band gap of solids through observation of the excitonic optical Stark effect (4–6), Rabi oscillations (7), and Fano resonances (8). Access to essential physical properties of the excitons such as their polarization (9) and relaxation time (10), as well as the presence of dark exciton states (11, 12), lays the foundation of modern optical excitonics (2). Advancement of exciton science and applications to the x-ray regime require the dynamic study of another class of quasiparticles that are formed between a core-hole in an atom of a solid and an excited electron generated by the absorption of x-rays (3). Ordinary absorption and photo-electron x-ray spectroscopies (14) can probe the core-hole excitations of solids, enabling a broad range of advances in condensed-phase physics (15), but fail to unambiguously identify quasiparticles in x-ray near-edge excitations (16–21) or to probe their dynamics. The establishment of x-ray excitons calls for the advancement of coherent spectroscopy for dynamic study of core-excitons.

Previous ultrafast studies in the condensed phase have exploited the near-edge excitation of solids as ultrafast probes to study attosecond valence electron dynamics in dielectrics (22) and semiconductors (23), as well as intraband currents (24) induced by intense few-cycle laser pulses. Yet, the study of the dynamics and nonlinear properties of the electron volt–wide core-hole excitations in solids requires a probe with attosecond resolution.

Here we combine an attosecond soft x-ray pump pulse with an attosecond optical probe pulse to perform near-edge spectroscopy of solids and thereby observe the quasiparticle character and measure the relaxation dynamics, as well as the exciton-photon coupling, the polarizability, and the effect of dark excitonic states. Soft x-ray study of solids in the coherent regime can take advantage of already recognized dynamic signatures of excitonic phenomena in optical studies to probe the character (excitonic or nonexcitonic) of the near-edge structure. These include the optical Stark effect and dynamic exciton bleaching that are manifested in pump-probe measurements as a dynamic energy shift of absorption resonances (4, 5) and an amplitude suppression (3, 25), respectively. In pursuit of such excitonic signatures, we chose to study the L$_{2,3}$ edge of the silicon atom in silicon dioxide (SiO$_2$) (~100 to 110 eV) as a prototypical system. The excitonic nature of this edge has been a matter of controversy (16, 17, 21). Moreover, the Auger decay ensuing from excitation of the L$_{2,3}$ edge occurs on a time scale (26) commensurate with the characteristic frequency of optical phonons (27) or molecular vibrations excited by the attractive force of the core-hole to neighboring atoms, giving rise to many-body-dominated relaxation phenomena (28–30) that have hitherto remained inaccessible.

In our experimental scheme (Fig. 1 and supplementary text section 1), a soft x-ray (E$_{x\text{-ray}}$ ~105 eV) attosecond pulse (Fig. 1A, magenta beam and waveform) lasting approximately ~τ$_{\text{x\text{-ray}}}$ ~200 as was used to excite the L$_{2,3}$ edge of Si in poly-crystalline SiO$_2$ nanofilms (thickness ~125 nm). A representative absorption spectrum recorded by the apparatus is shown in Fig. 1B (blue line) and is juxtaposed with its high-resolution counterpart (red dashed line, Fig. 1B) acquired for the same samples at a synchrotron source (Physikalisch Technische Bundesanstalt, PTB); A and A’ in Fig. 1B mark near-edge absorption peaks, earlier identified as core-valence transitions from spin-orbit states of the 2p orbital of Si (28). A third, substantially broader (~1.8 eV) spectral peak—marked as B in Fig. 1B—is often attributed to transitions from the same 2p orbital to the conduction band of SiO$_2$ and is more rarely assigned an excitonic character (17, 28).

To probe the coherent dynamics following the soft x-ray electronic excitation of the system in real time, an optical attosecond pulse (OAP) (peak field strength: F = 0.5 V/Å) (Fig. 1A, yellow line) (31) was used to dress the rapidly relaxing electric dipoles induced in the system by the soft-x ray attosecond pulse. We recorded transient absorption spectra as a function of the delay between the x-ray and optical pulse and composed transient absorption spectrometers for a delay range spanning several femtoseconds (Fig. 1C).

A close inspection of the transient absorption spectra in Fig. 1C permits the identification of excitonic signatures encoded in the dynamics of each absorption peak. The transient energy shift (dashed black line in Fig. 1C) of peaks A+A’ is a typical manifestation of the dynamic excitonic Stark effect (5, 6, 25, 32), whereas the conspicuous, amplitude suppression of peak B is the dynamic signature of exciton bleaching (25). The notion of an exciton character of the near-edge x-ray excitation of Si in SiO$_2$ is further indicated by the monotonic increase in the energy shift of peaks A+A’ and the decrease in the amplitude of peak B as a function of the field strength of the optical attosecond probe (Fig. 1D) in analogy to earlier studies of these phenomena in optical excitons. The signatures of the excitonic character of the L-edge can also be recognized in the differential absorption spectra (Fig. 1E) by the formation of dispersive spectral profiles for the Stark effect (Fig. 1F) and the negative differential absorption for bleaching, respectively.

To associate our findings with the current understanding of electronic structure of the Si-L$_{2,3}$ edge in SiO$_2$ (16, 17), we modeled the interaction of optical attosecond and soft x-ray pulses with SiO$_2$ as summarized in Fig. 2 and the supplementary text, using the semiconductor Bloch equations (SBEs) (25) on a basis of electronic states describing the near edges as calculated by density functional theory (DFT) simulations (fig. S1). The simulated density of states (DOS) (Fig. 2A) reveals that s-, p-, and d-like levels, as well as a dense continuum of states, practically dominate the Si-L$_{2,3}$ edge. Energetically, and in agreement with earlier studies, we can assign the A peaks to s-like excitons (red line), while peak B can be associated with d-like excitonic states (violet line). We accounted for the infinite effective mass of the 2p core level of Si by modeling it as a dispersion-free band (33). For simplicity, we modeled s states (peaks A and A’) as a single band (Fig. 2B). We introduced the continuum states into the model by the addition of a fourth band (green cloud). The excitonic character of the system was incorporated in our simulations by introducing Coulomb interactions to yield excitons (25) from each of the above bands (see also section 3 of the supplementary text).

The soft x-ray pulse drives transitions from the silicon 2p level to s and d excitons (violet arrows, Fig. 2B). Although p excitons (yellow line, Fig. 2A) contribute appreciably to the total state density of the system (Fig. 2A, blue line), their direct population from the 2p core is selection-rule prohibited, and thus they constitute dark excitonic
The excitonic character of the resonant states, but quantitative physical information is still lacking. To gain access to this information, we undertook reconstruction of the recorded differential absorption spectrograms (Fig. 1E) and retrieved relevant physical quantities. 

To this end, we modeled the absorption of soft x-rays in solids directly in the time domain. The electronic dipole \( d_s(t) \) induced by the absorption of the x-ray pulse (29, 34) can be expressed as 

\[
d_s(t) \sim \theta(t) e^{-\alpha t} e^{i\omega_0 t} e^{i\omega t t}
\]

where \( \alpha_0 \) is the transition energy with respect to the core level (2p), \( \nu/\hbar \) represents the inverse Auger lifetime of the core-hole of Si, \( t \) is time, and \( \theta(t) \) is the Heaviside function. The first three terms describe free induction decay of the excited dipoles characteristic for atomic systems, resulting in Lorentzian line shapes in the spectral domain. \( \phi(t) \) accounts for many-body relaxation dynamics resulting from scattering of the exciton with longitudinal optical (LO) phonons. The latter are created by the attractive (35) force of the core-hole to electrons in nearest-neighbor atoms resulting in the structural rearrangement of the system and can be expressed as (29)

\[
\phi(t) = \frac{(M_0^2/\omega_0^4)}{(2N + 1)(1 - \cos(\omega_0 t))} - i(\omega_0 t - \sin(\omega_0 t))
\]

Here, \( \omega_0 \) is the energy of the LO phonon in SiO₂, \( M_0 \) is the linear coupling strength between phonons and the excited electronic dipole, and \( N \) is the thermal phonon population (29). For SiO₂, the dominant LO phonon oscillations occur at \( \nu \sim 27 \text{ fs} \) (27), and the Auger decay of the Si 2p core hole has been assigned a value of \( h/\tau_{\text{Auger}} \sim 15 \text{ fs} \) on the basis of ordinary linewidth measurements (26). The validity of inferring the decay time of the core-hole from that of the exciton is established by the fact that the decay time of the exciton is limited to the natural Auger lifetime of the Si 2p core hole (35) as given by the expression 

\[
\tau_{\text{Auger}} = \frac{1}{N \rho \nu}
\]

where \( N \) is the thermal phonon population, \( \rho \) is the density of states near the Fermi level, and \( \nu \) is the LO phonon frequency. 

The experimental data and simulations were compared using a least-squares fit to the expression 

\[
\phi(t) = \frac{(M_0^2/\omega_0^4)}{2N + 1} \sum_{n=0}^{N} \frac{1}{(2n + 1)} (1 - \cos(\omega_0 t)) - i(\omega_0 t - \sin(\omega_0 t))
\]

Here, \( N \) is the thermal phonon population and \( \omega_0 \) is the LO phonon energy. 

The model discussed in the text consists of four terms: the first term describes the free induction decay of the excited dipoles characteristic for atomic systems, resulting in Lorentzian line shapes in the spectral domain. The second term describes many-body relaxation dynamics resulting from scattering of the exciton with longitudinal optical phonons. The third term accounts for many-body relaxation dynamics resulting from scattering of the exciton with longitudinal optical phonons. The fourth term accounts for many-body relaxation dynamics resulting from scattering of the exciton with longitudinal optical phonons. 

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isolated atoms from spectral measurements has been earlier verified by time-resolved measurements (36). To account for the effect of the optical field on the dynamics of the system, the electronic dipole induced in the system by soft x-ray and optical attosecond pulse can be expressed \((34)\) as:

\[
d_x(t) = \theta(t) e^{-\frac{i}{\gamma} E^2(t') dt'}
\]

where

\[
\phi_x(t, \tau) = -i \frac{\alpha}{2} \int_0^\infty E^2(t') dt' - \gamma \int_0^\infty E^2(t' - \tau) dt'
\]

is an optical gate.

Here \(\tau\) is the delay between pump and probe fields, \(\alpha\) is the polarizability, and \(\gamma\) accounts for amplitude reduction resulting from the optical field–induced coupling of the soft x-ray dipole with nearby electronic states (more detail on the reconstruction model is given in the supplementary text). We have verified that our model accurately describes nonlinearities in our experiments by testing its capability to reproduce the field-dependent shift of peaks A and A’ and the amplitude damping of peak B for a range of optical field strengths, as indicated by the dashed lines in Fig. 1D.

Figure 3 shows the experimental differential absorption spectrogram (Fig. 3A) and its reconstruction (Fig. 3B) based on the above-described model. The high fidelity of the reconstruction is underlined by the direct comparison of measured (Fig. 3C, red points) and reconstructed (Fig. 3C, blue lines) differential spectra at indicated (dashed lines in Fig. 3, A and B) representative delays. Figure 4A shows the unperturbed relaxation profiles of s and d excitons retrieved from the reconstruction in Fig. 3. S excitons (red and blue curves in Fig. 4A) relax over a time interval of \(T_a = 3.2 \pm 0.3\) fs; \(T_a = 2.3 \pm 0.2\) fs (\(\Delta T = 5.3 \pm 0.3\) fs; \(\Delta T = 3.8 \pm 0.2\) fs) and d excitons (violet curve, Fig. 4A), within \(T_a = 0.75 \pm 0.04\) fs (\(\Delta T = 1.25 \pm 0.04\) fs), measured at the full width at half maximum (FWHM) (and 1/e) of the intensity profile. Nevertheless, more important than directly accessing the fastest electronic relaxation dynamics to date is the capability of our approach for tracking physical properties of the system within these brief time intervals during which the interaction remains coherent. The considerably shorter relaxation times of d excitons (peak B) with respect to s excitons (peaks A and A’) result from a stronger coupling of these excitons with optical phonons. Indeed, the coupling strengths of exciton and LO phonon retrieved for s excitons is \(M_a = 0.158 \pm 0.006\) eV; \(M_a = 0.228 \pm 0.009\) eV, whereas \(M_a = 0.724 \pm 0.02\) eV is the coupling of the optical phonon with d excitons. The former agrees with earlier spectral domain estimations for the A and A’ peaks (s excitons), which predicted \(M_a < 1\) eV (28). This result is also compatible with the larger Bohr radius of d excitons compared to s excitons as revealed by our density functional theory (DFT) simulations (fig. S2), implying a wider phase space contributing to dephasing of d excitons.

Figure 4B to D, contrast the optical field–free relaxation of the s and d excitons (dashed lines) with those dynamically gated by the optical field, as retrieved in our reconstruction for a delay of \(\tau = 0.5\) fs between x-ray and optical pulses (solid lines). The optical attosecond pulse (yellow line) gates the dipole of s excitons by introducing a sizable phase shift [\(\phi_\text{opt} = 0.2\) rad] (red line), which is compatible with the prominent shift of the A peaks shown in our time-resolved traces (Fig. 1C) and simulations (Fig. 2C). The corresponding polarizability retrieved is \(\alpha_s = 3.6 \pm 0.2\) eV Å V\(^{-2}\); \(\alpha_s = 3.55 \pm 0.09\) eV Å V\(^{-2}\), and the amplitude damping is \(d_s = 0.17 \pm 0.01\); \(d_s = 0.00 \pm 0.03\) (where \(d_s = \exp(-\gamma \int_\tau^\infty E^2(t') dt')\)). By contrast,
The latter implies that the optical field acts primarily as an amplitude gate (compatible also with the observation of Figs. 1C and 2C) and results in the effective shortening of the relaxation time of the exciton to ~500 as. Note that owing to the nonlinearity underlying the interaction (see fig. S4 for different delay settings), the gating and control action of the optical field is restricted to the ~350-as time window of the most intense optical half cycle of the gate pulse.

We repeated the reconstruction with an extended alternative model (see supplementary text 4.2) to access the energy of the p exciton and the dipole matrix elements $\mu$ coupling it to the other excitons. We could retrieve an energy value of the dark exciton state of $E_r = 107.2 \pm 2$ eV, which is in good agreement with the predictions of the DFT simulation (Fig. 2A) ($E_r \sim 107.8$ eV) as well as estimations derived via multi-edge x-ray spectroscopies. The evaluated matrix elements linking s and p excitons are $\mu_{sp} = 1.5 \pm 0.2$ atomic units (au), $\mu_{sp} = 2.9 \pm 0.5$ au and $\mu_{dp} = 0.7 \pm 0.2$ au, respectively. The above data represent the complete characterization of the dark excitonic state and allow further estimations for the s-ground state of the core exciton.

The nonresonant polarizability can be estimated as $\alpha = \mu^2 / \epsilon_{sp}^2$ yielding a value of $\alpha_s \sim 40$ au; $\alpha_p \sim 235$ au. For a hydrogenic system, the nonresonant polarizability $\alpha$ and the Bohr radius $r_B$ are linked in atomic units as $\alpha = 2 \epsilon_{sp}^2 r_B^2$, where $\epsilon$ is the dielectric constant of SiO$_2$. The evaluation of the Bohr radius yields $r_B = 1.3 \pm 0.2$ au, which is the Bohr radius of the hydrogen atom. These results are in very good agreement with the radius of the s exciton evaluated from our DFT simulations ($r_B$) similar to $1.3 \pm 0.2$ au and suggest that our approach can probe the extreme confinement of the core-exciton within sub-unit-cell (for SiO$_2$), approximately dimensions directly from dynamic measurements.

This capability of probing ultrafast dephasing of excited electrons in bulk solids may also prove essential for understanding the role of dephasing in emerging photonic phenomena such as high harmonics generation. Thus, the knowledge of the polarizability of core excitons is an essential prerequisite for porting optical excitonic control of radiation (39) into the x-ray regime and realizing sub-optical cycle gates of x-ray radiation, an unexplored possibility of critical importance in free electron laser (FEL) technologies and their applications.
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A quick glimpse of the x-ray aftermath
X-rays pass through your skin to reveal the inner workings below. At the atomic scale, x-rays skip past valence electrons to grab hold of the core electrons closer to the nucleus. Moulet et al. used two successive, extremely short laser pulses (lasting less than a quadrillionth of a second) to initiate and then track this process in a sample of silica. This study uncovered the angular momentum character and relaxation dynamics of the excitons, or electron-hole pairs, ensuing from the x-ray absorption.

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