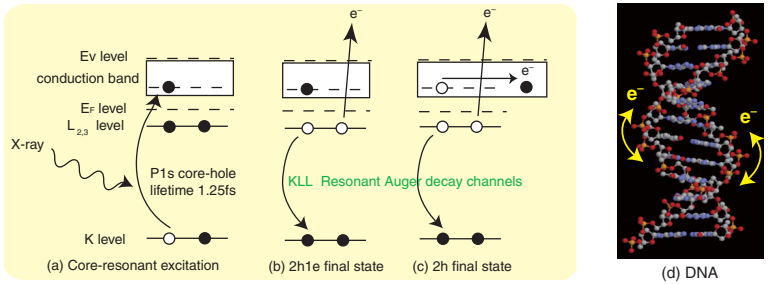
Unoccupied Conduction Band State with Attosecond Electron Delocalization through DNA Backbone

The conductivity of DNA is a key property for future applications as molecular wires, and for understanding the mechanisms of the detection and repair of damaged DNA in relation to the processes of cancer and aging. The partial density of states in the empty conduction band of the phosphate backbone sites in DNA has been probed using energy-dependent resonant Auger spectroscopy. The results show that genomic DNA with periodic backbones exhibits an extended state despite the separation of each phosphate group by an insulating sugar group. On the other hand, in antisense phosphorotioate DNA with an aperiodic backbone, the equivalent state is localized. Remarkably rapid electron delocalization occurs on a sub-femto/attosecond time scale, as estimated using the core-hole clock method.

Brillouin [1] proposed that the double-stranded sugar-phosphate backbones of DNA form conduction bands because of their quasi-one-dimensional periodic structures in which the electronic states are extended. To understand how electrons move through the DNA backbone, we have used X-ray absorption spectroscopy (XAS), which enables the selective excitation of the phosphorus 1*s* core electron to an empty orbital of the DNA backbone. Resonant Auger spectroscopy (RAS) is also used to monitor the conduction of an initially localized core-excited electron around the absorption atom [2]. In this method, the RAS spectra are interpreted based on two competing decay channels: core-hole decay and core-excited resonant electron delocalization. If the resonantly excited electron remains sufficiently long to be localized in the vicinity of a core-hole site during the core-hole decay, the decay process results in a final state of two holes with one electron (2h1e), a process known as "spectator Auger" decay [Fig. 1(b)]. In contrast, if it delocalizes to the conduction band prior to core-hole decay, the decay process results in a two hole final state (2h) "normal Auger" decay [Fig. 1(c)]. Consequently, for the case in which the timescale of delocalization is comparable to that of the core-hole decay, both the spectator and the normal Auger electrons can be detected. By quantifying the intensity ratio, one can measure the electron-delocalization time through the DNA backbone, τ_{ED} [Fig. 1(d)]. This is the so-called "core-hole-clock" method (see [3] for a review), in which the core hole acts as a fast internal clock.

The experiments were performed at BL-27A. The Auger spectra were recorded using a hemispherical analyzer. A typical P $KL_{2,3}L_{2,3}$ RAS of dry DNA (similar to wet DNA) at the t_2^* transition is shown in Fig. 2(a). Partial yields for the 2h1e and 2h Auger final states of wet DNA were obtained at each excitation energy from the peak areas for the dominant ($^1D_2$) and ($^1D_2$) t_2^* Auger electrons, respectively, shown in the XAS in Fig. 2(b). In the 2h yield spectrum, an intriguing peaked feature at ca. 2153.7 eV is observed, corresponding to a delocalized component of the partial density of states of t_2^* near E_F. This delocalized feature confirms that the t_2^* orbitals are extended along the direction of the phosphate backbone. A synthesized single-stranded phosphorothioate DNA oligomer (PS-oligo) was used as an example of a molecule with aperiodic backbones. The PS-oligo has one sulfur atom replacing a non-bridging oxygen atom in the phosphate backbone [Fig. 2(d)]. The



(d) DNA

Figure 1
(a) A phosphorus 1s core electron is excited into an unoccupied state in the conduction band. (b) Spectator Auger final state (2h1e) caused by localization of the electron to the core-hole site. (c) Normal Auger final state (2h) caused by delocalization of the electron to the conduction band coupling to the continuum. (d) DNA shown with electron motion along the backbone.

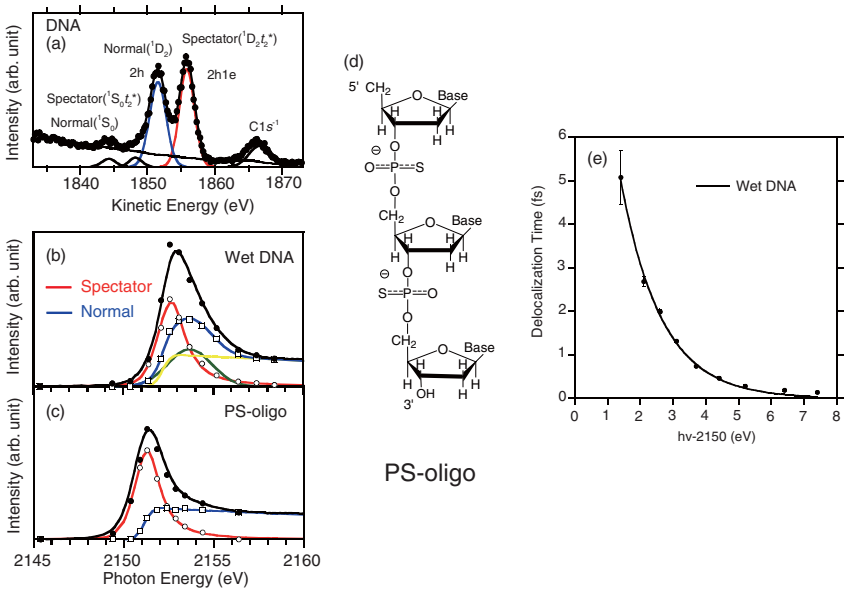


Figure 2
Typical P KLL resonant Auger spectrum of dry DNA at 2152.9 eV (a). Integrated intensities of the spectator (red lines, open circles) and normal (blue lines, open squares) Auger components for (b) wet DNA and (c) PS-oligo. (d) Molecular structure of PS-oligo containing phosphorothioate linkages. (e) Excitation energy dependence of the electron-delocalization time τ_{ED} for wet DNA. The error bars show ±1σ, and the solid lines are exponential fits to the datapoints.

P-S bonds cannot be aligned parallel to each other, resulting in an aperiodicity of the backbone. In contrast to DNA, the 2h yield spectrum shows a step-like ionization continuum [Fig. 2(c)]. The lack of a delocalized band peak suggests that the orbitals remain localized at each phosphate molecule. However, it should be noted that the core-hole potential can promote electronic localization without increased screening of the core hole, and it is important to take into account these core-hole effects.

To investigate how the fast electron delocalization occurs through the DNA backbone, τ_{ED} has been investigated using the core-hole clock method. The relationship between τ_{ED} and the relative intensity of the 2h and 2h1e final states can be described as [3] $\tau_{ED} = \tau \times (I_{2h1e} / I_{2h})$, where τ is the core-hole lifetime. I_{2h1e} and I_{2h} respectively represent the intensities of the spectator and normal Auger components. The P 1*s* core-hole lifetime of 1.25 fs [4] is used for τ. The τ_{ED} of wet DNA is shown as a function of excitation energy in Fig. 2(e). In this system, the energy dependence is expected to result from the tunnelling barrier and the density of states in the conduction band. τ_{ED} is found to decrease with increasing excitation energy.

To date, it has been widely accepted that the DNA base stacks explain conduction through the DNA wire, but the mechanism remains unclear. Complementary conduction through the phosphate backbones may give a new insight into the mechanism. Finally, we emphasize that the core-hole-clock method can serve as a new tool for probing attosecond electron-delocalization dynamics along one-dimensional molecular chains without the need for electrodes.

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BEAMLINE

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