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33. $q_l(i)$ is a second-order rotational invariant of the $(2l + 1)$–component bond-order parameter $\mathbf{q}_l(i)$ for particle i and is defined by

$$q_l(i) = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right]^{\frac{1}{2}}$$

$w_l(i)$ is a third-order rotational invariant defined by

$$w_l(i) = \sum_{\substack{m_1,m_2,m_3 \\ m_1+m_2+m_3=0}} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \times q_{lm_1}(i) q_{lm_2}(i) q_{lm_3}(i)$$

where $(:::)$ stands for a Wigner $3j$ symbol.
34. The histograms for fcc, bcc, and hcp order were obtained from computer-generated crystal data. Random fluctuations were added to the particle positions in such a way that the width of the first peak of $g(r)$ for the computer-generated data matched the experimental value. The bond-order histograms were then calculated in the same way as for particle positions from a measurement. The liquid histogram was taken from observations shortly after shear melting, when the sample was in the liquid state.
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Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure

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The determination of the structure of transient molecules, such as photoexcited states, in disordered media (such as in solution) usually requires methods with high temporal resolution. The transient molecular structure of a reaction intermediate produced by photoexcitation of NiTPP-L$_2$ (NiTPP, nickeltetraphenylporphyrin; L, piperidine) in solution was determined by x-ray absorption fine structure (XAFS) data obtained on a 14-nanosecond time scale from a third-generation synchrotron source. The XAFS measurements confirm that photoexcitation leads to the rapid removal of both axial ligands to produce a transient square-planar intermediate, NiTPP, with a lifetime of 28 nanoseconds. The transient structure of the photodissociated intermediate is nearly identical to that of the ground state NiTPP, suggesting that the intermediate adopts the same structure as the ground state in a noncoordinating solvent before it recombines with two ligands to form the more stable octahedrally coordinated NiTPP-L$_2$.

Photoexcited states of molecules are often studied with "pump-probe" methods, in which a short optical pulse excites the ground state, and a second probe pulse interrogates the excited state. For structural studies, substantial progress has been made in generating ultrashort x-ray pulses (*1–4*) that have been used to obtain time-resolved x-ray diffraction information with picosecond resolution (*5–7*). Because many light-driven processes occur in disordered media, techniques that do not rely on the long-range order of a system must be developed. The approach of laser pump/x-ray probe x-ray absorption fine structure (XAFS) was proposed earlier (*8–10*), and transient molecular structures, generated in light-induced processes, were captured without using the temporal resolution of the source (*11–19*).

Here we present time-domain laser pump/x-ray probe XAFS studies using x-ray pulses from a third-generation synchrotron source. (The experiments were conducted at a wiggler beamline at the Basic Energy Sciences Synchrotron Research Center at Argonne National Laboratory's Advanced Photon Source.) Although the duration of the x-ray pulses (100 ps at full width at half-maximum) is too long to follow atomic displacements due to the photoexcitation, it is suitable for capturing intermediate structures with subnanosecond resolution. We are able to take "snapshots" of molecules when the population of the laser-generated transient species reaches a maximum; in this case, the species is a reaction intermediate with a 28-ns lifetime that results from the photodissociation of NiTPP-L$_2$ (NiTPP, nickeltetraphenylporphyrin; L, piperidine) in solution (Fig. 1A).

The photoinduced processes of hemelike porphyrin derivatives are examples of how, through electron transfer, the coordination geometry of a metal ion is altered by the electronic structure of its macrocycle ligands. These molecules can serve as models for oxygen transport, catalysis, and the photoinduced redox reactions. According to previous studies (*20–22*) in a weakly coordinating or noncoordinating solvent, the $3d^8$ electrons of the Ni(II) ion in the square planar geometry of NiTPP adopt a singlet spin state $^1(3d_{z2})^2$, S_0, whereas these electrons in the octahedral geometry of NiTPP-L$_2$ prefer the triplet spin state $^3(3d_{x2\text{-}y2}, 3d_{z2})$, T_0. This difference reflects the response of the $3d_{x2\text{-}y2}$ and $3d_{z2}$ orbitals in the square planar and octahedral ligand fields. Starting with NiTPP-L$_2$, a laser pump pulse induces an electronic transition from the triplet ground state, T_0, to an excited triplet state, T^* (Fig. 1B). This state decays and undergoes intersystem crossing to an excited singlet state, S^*. This excited state ejects two ligands L to produce the square planar geometry (*20–22*). If the solvent were noncoordinating or weakly coordinating, this reaction sequence would be completed. However, in a strongly coordinating solvent, S_0 is unstable and the system will return to T_0, by recombining with two piperidine ligands to form an octahedrally coordinated NiTPP-L$_2$ (Fig. 1). The transient structures involved in this recombination are not known. A penta-coordinated NiTPP-L molecule could be involved in the recombination, the square planar NiTPP could return to T_0 via a concerted axial chelation with two piperidine molecules, or an intermediate square pyramid NiTPP-L structure could be important. Because it is difficult to identify a unique optical absorption spectrum for each possible intermediate involved in photodissociation, transient optical absorption spectra of NiTPP in coordinating solvent alone are not sufficient to identify the intermediates.

The excited-state dynamics of NiTPP-L$_2$ have been studied by ultrafast optical transient absorption and Raman spectroscopy (*20–25*). The intersystem crossing from T^* to S^* and the subsequent dissociation to S_0 occur in less than a few hundred picoseconds (*22*). In a strongly coordinating solvent at room temperature, this state of NiTPP has a lifetime of 28 ns, because it must react with two piperidine molecules to reform NiTPP-L$_2$. We can therefore use x-ray pulses from a synchrotron source to determine the local structure of these intermediates and compare them with the structure of ground state NiTPP. In addition, it is possible to determine whether an intermediate species with only one axial ligand is present (*22*). The experiment was

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carried out with a pseudo-asymmetric fill mode of the electron bunches in the storage ring (*26*), which generates an isolated x-ray pulse cluster containing six pulses within 14.2 ns (with 2.84 ns separation between adjacent pulses) centered in a window of 3160 ns, well separated in time from other x-ray pulses. A picosecond laser pulse with a 5-ps duration at 351 nm coincident with the first x-ray pulse in the pulse cluster induces a π-π^* transition in the porphyrin macrocycle. This excitation leads to dissociation of the axial piperidine ligands in NiTPP-L_2 within a few hundred picoseconds.

The XAFS spectra (Fig. 2) for the laser-pumped NiTPP-L_2, along with those of the ground states NiTPP-L_2 and NiTPP, show the following features. A distinct shoulder at 8.340 keV appears in the x-ray absorption near-edge structure (XANES) (Fig. 2A) of the ground state NiTPP, which is attributed to the 1*s*-to-4p_z transition in a square planar transition metal complex (*27*) that would not be seen in an octahedral or a square pyramid complex. This shoulder feature also appeared in the XANES region of the laser-pumped sample, but with a lower amplitude, and disappeared when the pump laser beam was blocked or when the detector was gated long after the ground state recovery. Therefore, the appearance of this feature in the XANES spectrum of the laser-pumped sample indicates that a transient square planar NiTPP-like structure has been created by the laser. The XANES spectrum of the laser-pumped solution sample can be reconstructed by mixing the ground state NiTPP-L_2 and NiTPP-like spectra with a ratio of approximately 7:3. The XAFS spectrum of the laser-pumped sample also exhibits differences from the spectra of the starting octahedral NiTPP-L_2 and the ground state NiTPP (Fig. 2B). Fourier-transformed XAFS spectra (Fig. 2C) clearly show that the average distance from the Ni ion to the nearest neighbor N atoms for the laser-pumped sample falls between those of NiTPP and NiTPP-L_2 at their respective ground states. The XAFS spectra for the Ni-N peak (Fig. 2C) were fit to obtain coordination number and bond length information (*28*, *29*). Table I displays the fitting results. Each spectrum of the ground state NiTPP or NiTPP-L_2 can be fit with a single Ni-N distance. The average Ni-N distance of 1.91 Å for NiTPP agrees with its crystal structure (*30*), whereas that of 2.09 Å for NiTPP-L_2 is slightly shorter than an average distance of 2.11 Å from the crystal structure (*31*) The discrepancy between the solution and the crystal structures may arise from the effect of crystal packing and the dynamic nature of the molecular structure in solution at room temperature (*31*).

The nearest neighbors for the laser-pumped sample could be best described by two distances of 2.10 ± 0.02 Å and 1.92 ± 0.02 Å, with a relative ratio of 3.2:1. This ratio is only slightly less than an expected value of 3.5:1 and is within the experimental errors for a 30% yield of the square planar intermediate as estimated from the XANES spectrum, which is in agreement with the transient optical absorption measurement, where the pump pulse with the same photon flux depleted 28% of the peak absorption by the ground state NiTPP-L_2. Based on the structures of a previously studied penta-coordinated Ni bacterial chlorophyll that have a similar coordination environment as NiTPP, the Ni-N bond length increases from 1.95 to 2.04 Å when the coordination of Ni changes from a square planar to a square pyramid geometry (*32*). Thus, if there were a substantial amount of NiTPP-L present, the nearest neighbor distances would not resemble so closely those for NiTPP and NiTPP-L_2, and the fraction of the NiTPP intermediate obtained from fitting the XANES would not agree so well with the two-distance fitting of the nearest neighbors from the XAFS spectra. In addition, the pre-edge peak of *1s*-to-*3d* transition is not enhanced, as it would be in the noncentral symmetric geometry of a square pyramid NiTPP-L. Therefore, the photoinduced intermediate formed during the first 14 ns after the laser pulse is primarily the square planar NiTPP, with an average nearest neighbor distance that is almost identical to the ground state NiTPP. This result rules out the presence of a substantial amount of transient NiTPP-L. However, if the yield of NiTPP-L were less than 10% (*22*), only 3% of the total number of molecules, it would not have been detected. Moreover, if the lifetime of NiTPP-L were much shorter than the 14-ns duration of the superbunch, it would not have been observed. These results agree with the

Table 1. The nearest neighbor distances. For details of data analysis, see the supplementary materials (*33*).

Compound	Coordination number	Bond length (Å)	Debye-Weller* factor (Å^2)
NiTPP	4.0 ± 0.5	1.91 ± 0.02	0.003
NiTPP-L_2	6.0 ± 0.5	2.09 ± 0.02	−0.003
Laser-pumped NiTPP-L_2	5.7 ± 0.5	2.10 ± 0.02	0.004
	1.8 ± 0.5	1.92 ± 0.02	0.005

*Relative to the nearest neighbor distance distribution in the crystal structure.

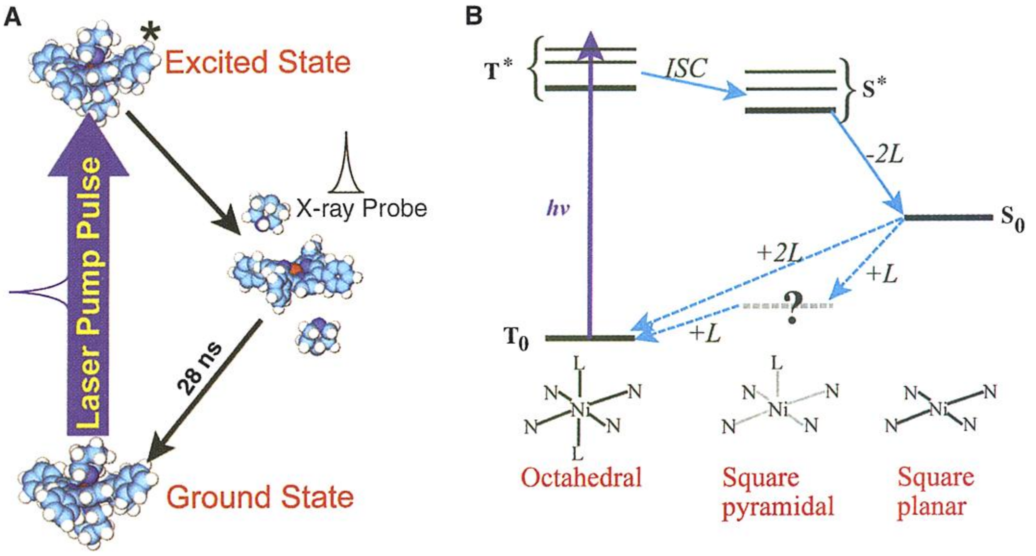

Fig. 1. (**A**). A laser pump pulse induces an electronic transition from the ground state NiTPP-L_2 to its excited state that triggers the photodissociation of the axial ligands. The structure of the photodissociated intermediate with a 28-ns lifetime is probed by x-ray pulses before the recombination reaction occurs. The details of the experiments are described in the supplementary materials (*33*). (**B**) Reaction path of photodissociation of NiTPP-L_2 (only the nearest neighboring atoms that are chelated with Ni are shown), where the ground triplet state T_0 is photoexcited to upper triplet states T^* (representing a group of possible triplet states). T^* then undergoes intersystem crossing to S^*, which could occur very quickly, and, finally, ejection of two ligands to form S_0. This transient species was captured by the laser pump/x-ray probe XAFS experiment before it returned to the more stable T_0 state of NiTTP-L_2 (see text for a detailed description of the reaction path).

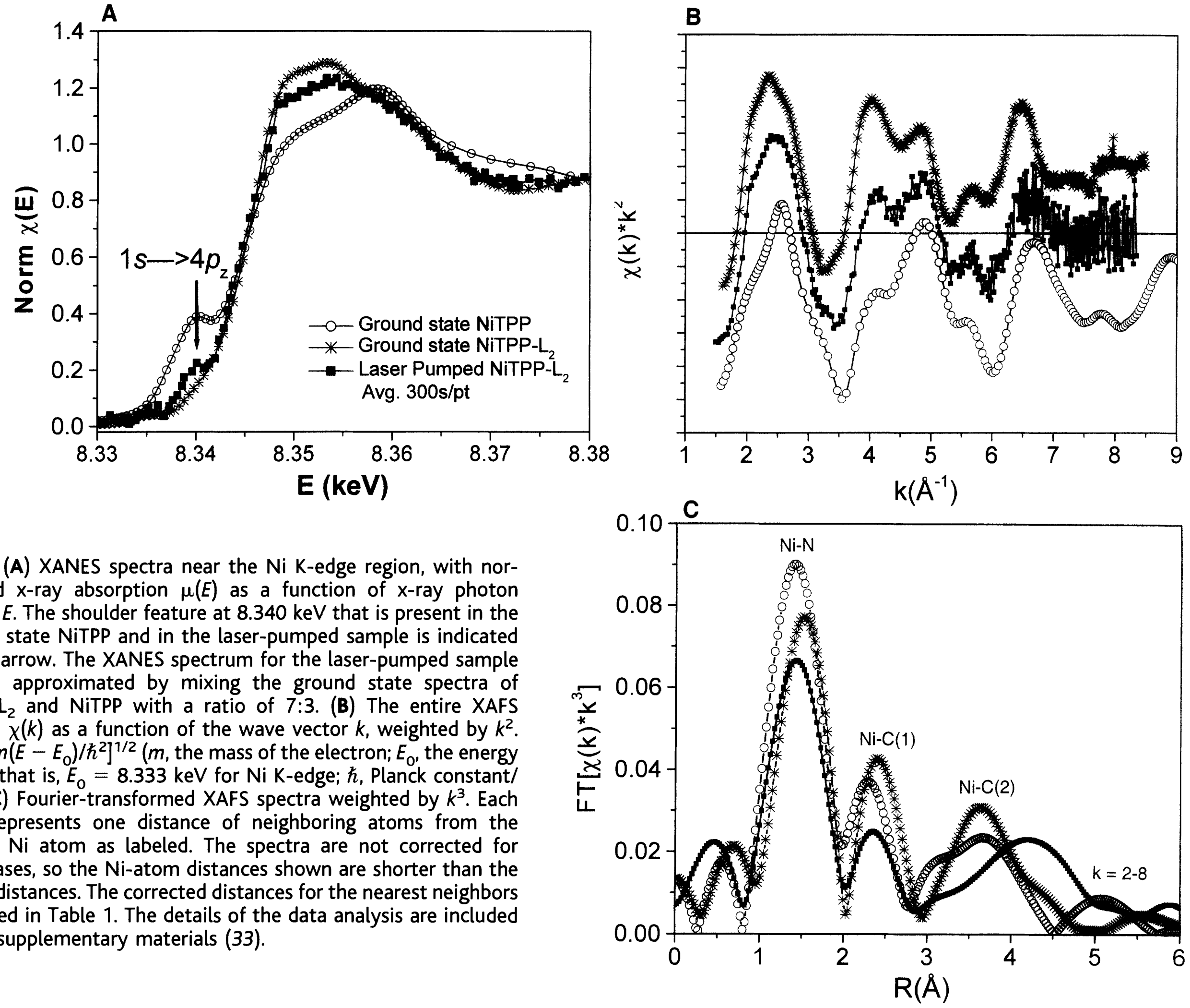

Fig. 2. (**A**) XANES spectra near the Ni K-edge region, with normalized x-ray absorption $\mu(E)$ as a function of x-ray photon energy E. The shoulder feature at 8.340 keV that is present in the ground state NiTPP and in the laser-pumped sample is indicated by the arrow. The XANES spectrum for the laser-pumped sample can be approximated by mixing the ground state spectra of NiTPP-L$_2$ and NiTPP with a ratio of 7:3. (**B**) The entire XAFS spectra $\chi(k)$ as a function of the wave vector k, weighted by k^2. $k = [2m(E - E_0)/\hbar^2]^{1/2}$ (m, the mass of the electron; E_0, the energy origin, that is, E_0 = 8.333 keV for Ni K-edge; $\hbar$, Planck constant/2π). (**C**) Fourier-transformed XAFS spectra weighted by k^3. Each peak represents one distance of neighboring atoms from the central Ni atom as labeled. The spectra are not corrected for the phases, so the Ni-atom distances shown are shorter than the actual distances. The corrected distances for the nearest neighbors are listed in Table 1. The details of the data analysis are included in the supplementary materials (*33*).

previously proposed reaction path for the photodissociation of NiTPP-L$_2$ with a triplet ground state (*22*).

Our results demonstrate that laser pump/x-ray probe XAFS using x-rays from a third-generation synchrotron source provides a new and powerful approach to monitor transient molecular structures in disordered media. For many metal-containing photoactive molecules, the electronic transition that governs reactivity is the metal-to-ligand charge transfer transition, which moves electrons from the metal ion to the ligands and produces a transient change in the oxidation state of the metal. This change may be detected by XAFS spectroscopy if the laser pump/x-ray probe technique can be applied. Inevitably, such transient oxidation changes could cause atomic displacements as well, which could also be detected by XAFS. Although the superbunch used in this experiment had six consecutive pulses within a 14-ns time span, which limited the time resolution of this experiment, a single-pulse superbunch is scheduled for future operation at the Advanced Photon Source and will allow us to capture intermediate structures on even shorter time scales.

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