

Ultrafast Selected Energy X-ray Absorption Spectroscopy (USEXAS) with a Laser-Driven X-ray Source

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ABSTRACT

A laser driven electron x-ray source (LEXS) emitting tungsten L_{α} lines has been built based on a high repetition rate, terawatt laser system. The L_{α} characteristic lines overlap with the absorption edge of Ni near 8333 eV. Using this x-ray source, the x-ray absorption spectra near the absorption edge of different Ni compounds have been measured. We term this new method “ultrafast selected energy x-ray absorption spectroscopy (USEXAS).” It provides an efficient way to study ultrafast reaction dynamics of many metal complexes in solution.

Keywords: ultrafast x-rays, x-ray absorption spectroscopy, terawatt lasers, ultrafast reaction dynamics, atomic motion

1. INTRODUCTION

The advancing high power laser technologies have enhanced our ability to build more compact size terawatt lasers.⁽¹⁻³⁾ These new lasers have in turn made it easier to implement a special type of x-ray sources, the laser-driven electron x-ray sources (LEXS).⁽⁴⁻⁶⁾ The development of LEXS runs a parallel path to the development of laser-plasma x-ray sources for plasma and fluid diagnoses. The plasma x-ray sources have been studied for over three decades, and have been reviewed in many excellent articles.^(7,8) Recently, elaborate schemes have been used to produce ultrafast hard x-ray pulses of hundreds of femtoseconds,⁽⁹⁻¹³⁾ and various diffraction and absorption measurements have been performed with these ultrafast laser based sources.^(5,6,14,15)

A LEXS consists of two major components, a terawatt laser system and an x-ray target apparatus. The terawatt laser is necessary for generating energetic electrons (from a few keV to a few hundred keV) of subpicosecond pulse length, and special targets are needed for the long operation hour generation of desired x-ray wavelengths. With these LEXS, one can develop various x-ray absorption spectroscopy and diffraction methods.

X-ray absorption spectroscopy (XAS), which includes both extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge spectroscopy (XANES), has been used to obtain structures of amorphous and crystalline materials for many decades.⁽¹⁶⁾ It is essentially a local diffraction approach which can be used to study short range order problems. EXAFS is now a well-established method because of the straightforward relationship between the

modulation in the absorption spectra and the interatomic distances, coordination numbers, and distance disorders. EXAFS mainly relies on photoelectrons with kinetic energies over 50 eV. It is thus generally accepted that the pattern of EXAFS is largely determined by the atomic configuration of the material studied. Theories of EXAFS have already extended into the ultrafast region. ⁽¹⁷⁾ However, due to the small modulation amplitudes in the EXAFS spectra, high S/N ratio data is needed. In many cases, synchrotrons are necessary to acquire high quality data. ⁽¹⁸⁾ On the other hand, XANES carries much larger modulations and is very sensitive to small changes in atomic and electronic configurations even though it is more difficult to interpret. The range of energies of the photoelectrons affecting XANES includes two regions: pre- (between a few eV below and above the edge) and near edge (from the edge to ~ 50 eV above the edge). Therefore, both EXAFS and XANES are useful for understanding reaction dynamics (which is a short range order problem) by revealing the dynamics of atomic and electronic motions.

There are several distinctive advantages to using LEXS to investigate atomic motion via scrutinizing the changes in x-ray absorption spectra during reactions. First, if it is possible to monitor a spectrum in both the pre/near edge and the extended regions, one can then separate electronic motion from atomic motion. Second, XAS on the ultrafast time scale should be self-referenced, i.e., only net changes occurring to the static structure, i.e., the dynamic absorption spectrum, are needed for interpretation. The static structure can be studied and interpreted separately, for example, using synchrotron sources.

Although broadband x-ray pulses can be produced from a LEXS through processes such as Bremsstrahlung radiation or plasma (Stark) broadening from thermal sources, it is important to realize their limits. The Stark broadening is unlikely to cover the energy range or the equivalent reciprocal space needed for an accurate Fourier Transformation. For example, a bandwidth of several hundred to over a thousand eV is needed for Fourier transforming an EXAFS pattern in the multiple keV energy range into the real space. Bremsstrahlung radiation, on the other hand, is two to three orders of magnitude weaker than the characteristic emission in the region of hard x-rays (~10-100 keV), and data acquisition time becomes a concern when Bremsstrahlung is used for absorption measurements. Therefore, one of the advantages of using LEXS in x-ray absorption spectroscopy lies in the use of intense characteristic emission that covers important spectral regions in which the temporal evolutions of the absorption spectrum can help us gain understanding of reaction dynamics. As a result, selected energy ranges can be probed with the ultrafast characteristic x-ray pulses, and we call this method ultrafast selected energy x-ray absorption spectroscopy, or USEXAS. The principle of USEXAS has been described before, and here we will present the experimental data on the tungsten target and the absorption measurements. ⁽¹⁹⁾

In the following, we will briefly describe the laser system and the x-ray target apparatus. Data on Ni compounds will be presented.

2. LASER AND X-RAY GENERATION

We built a terawatt laser in our lab. It has been described in detail in two other publications ^(1,19). Briefly, the FWHM of the final pulses after compression was 38 fs after grating angles and separation were optimized, and the pulse energy was 55 mJ/pulse at 50 Hz. The central wavelength was 790 nm.

When focused on a tungsten target, the laser beam can produce both Bremsstrahlung and characteristic x-ray radiation. We designed a tungsten

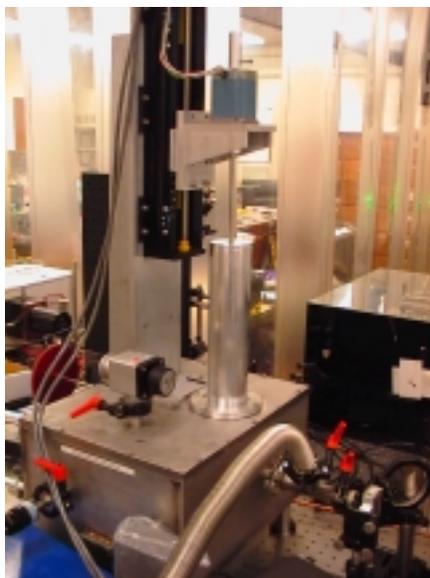


Figure 1. Tungsten rod target

rod target (see Figure 1) that provided a run time of a few tens of hours. A detailed description will be given elsewhere⁽²⁰⁾. This apparatus was similar to the wire target we presented previously, although a tungsten rod replaced the wire as the target. Using this target, $L_{\alpha 1}$ and $L_{\alpha 2}$ line emission were produced and measured with an x-ray detector (deep depletion PI-LCX 576, Roper Scientific), as shown in Figure 2. The pattern was obtained after the x-rays were diffracted by a GaAs (111) single crystal (Virginia Semiconductor). The ratio of the peak intensities was about 10:1, similar to the theoretical prediction.⁽²¹⁾ The FWHM of the line profile was about 9 eV, broader than the natural line width by ~ 2 eV. This broadening was due to the imperfection of the crystal and the non-point like x-ray source size. The total flux of the two L_{α} lines was about 7×10^9 photons/(4π Sr s). Such intensity was only a fraction of the K_{α} of Cu, due to the lower fluorescence yield of tungsten L lines.

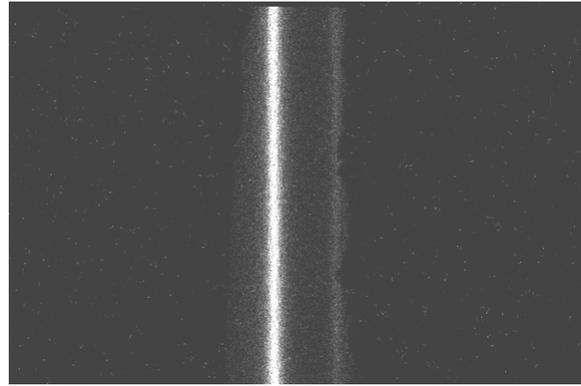


Figure 2. Tungsten $L_{\alpha 1}$ (left) and $L_{\alpha 2}$ lines.

We also investigated the dependence of the x-ray yield on the laser intensity of the prepulse/pedestal and the grating separation of the compressor. The latter controlled both the duration of the laser pulses and the amount of chirp. The prepulse/pedestal level was adjusted using the Lasermatrix (Model 5046, Fast Pulse Technology, Inc.). Figure 3 shows the results. In Figure 3, the two parameters (prepulse/pedestal level and the grating separation) were changed as a function of time, and the 3/2 harmonics (left panel) and the x-ray intensity (right panel) were monitored. In the first period (0 to 20 sec), the prepulse/pedestal was set to low (< 2 mV on the oscilloscope) and the grating distance was set so the optical pulse was several hundred femtoseconds long. The second period (20-90 sec) corresponds to almost the maximum level of prepulse/pedestal (20 mV) while keeping the grating separation the same. In the third section (90-110 sec), the grating separation was again set the same, and the prepulse/pedestal level was adjusted to the minimum (0 mV). In the fourth period (110-180 sec), the grating separation was changed to make the pulses slightly longer while the prepulse/pedestal level was kept the same. In the last period (180-200 sec), the grating separation was set to produce the shortest optical pulses with the maximum prepulse/pedestal. The green light was intense, so was the light near 750 nm. However, the x-ray intensity was low.

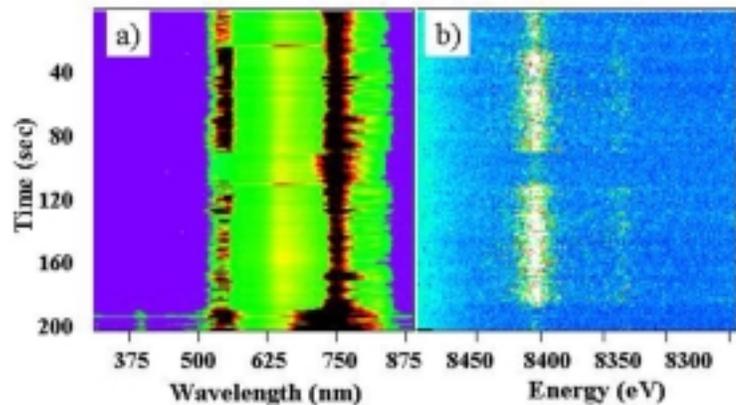


Figure 3. Simultaneous monitoring of the visible light (3a) from the source and the x-ray intensity (3b). In 3b, the left line represents $L_{\alpha 1}$.

It is clear that the highest L_{α} line intensity was achieved when the pulse duration was not the shortest, and the pedestal/prepulse was at a moderate level. These simple optimizations indicated that the optimal laser intensity was below the one the current laser might provide when the shortest pulse and smallest focal spot size were used. Further optimization of all four parameters is needed to obtain the desired x-ray pulses, whether they are the shortest or the brightest.

3. USEXAS SPECTRA OF NI COMPOUNDS

Since USEXAS relies on a match between the emission lines of certain elements and the absorption edge of the interested elements, it is worth pointing out that it is not a method that can be applied to studying every element. Even so, the many elements that can be studied with USEXAS all possess interesting ultrafast reaction dynamics. For example, Cs and Ru can be studied with the characteristic lines from Pd and Pr. Ni complexes can be investigated by line emission from W. Furthermore, Bremsstrahlung radiation from LEXS can be used to study other elements, although data acquisition times will be significantly longer.

By passing the tungsten L_{α} line x-rays through a Ni compound, either in the solution or solid phase, we can obtain a USEXAS profile. Figure 4 shows an absorption spectrum obtained on a NiTPP film of 200- μm thickness. 5 min data acquisition was used to obtain the direct x-ray spectrum (I_0). 30 min total data acquisition time was used to obtain the x-ray spectrum (I) after absorption by the sample. The absorbance was obtained using $A = -\ln(I/I_0)$. A theoretical (i.e. from synchrotron measurements) profile for this compound is also given (the smooth solid line overlaying on top of the noisy experimental data).⁽²²⁾ Since the absorption edge is close to the peak of $L_{\alpha 2}$ line, the S/N ratio is lower than that at the peak of $L_{\alpha 1}$.

It is clear that the absorption edge can be detected with this method. We are working on getting much higher S/N absorption profiles by increasing the data acquisition time, optimizing the sample thickness and the x-ray yield.

4. DISCUSSION

In USEXAS, two or more regions of the absorption spectrum in both the pre/near edge and the extended regions are monitored simultaneously and on the ultrafast timescale. For example, based on the discussion in Section 1, one can conclude that the absorption spectra in the extended region should remain the same during pure electronic motions. Therefore, if both the pre/near and the extended regions are monitored, we will be able to differentiate atomic motion from electronic motion. Figure 4 shows

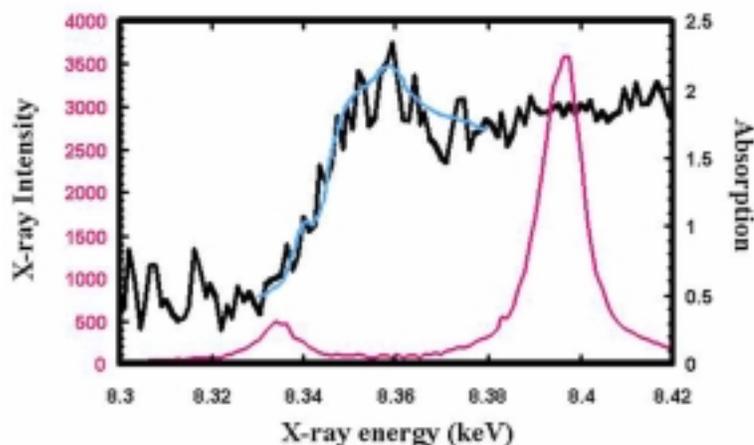


Figure 4. Absorption spectrum of NiTPP from tungsten $L_{\alpha 1}$ (the peak on the right) and $L_{\alpha 2}$ lines. The smooth solid line overlaying on the experimental data is the result from synchrotron measurements.

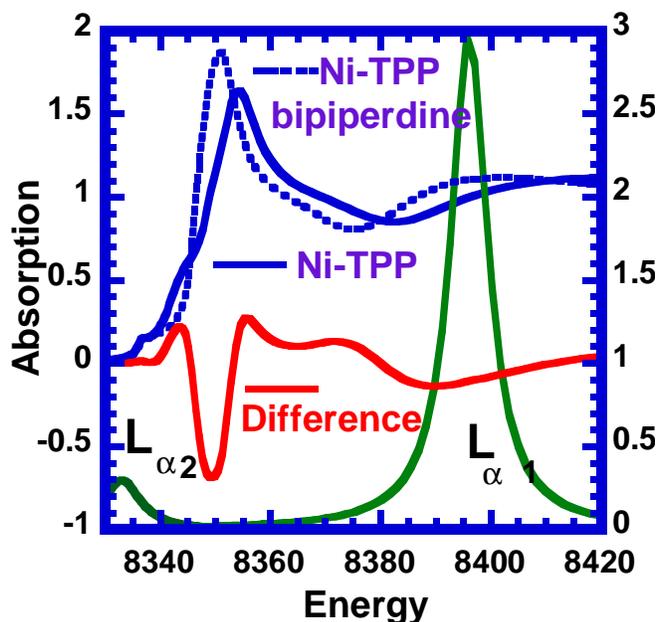


Figure 5. FEFF calculations of XAS patterns of NiTPP bipiperidine and NiTPP. Also shown are the $L_{\alpha 1}$ and $L_{\alpha 2}$ lines of tungsten.

USEXAS spectra in both regions.

The static measurement shows that one can use USEXAS to probe chemical dynamics in the condensed phase. A specific example, the photodissociation dynamics of the axial ligands in complexed Ni porphyrins, can be used to illustrate the principle of this method. The Ni system has been used to mimic metalloproteins, and nanosecond x-ray absorption measurements have been performed on this system.⁽²²⁾ The XAS patterns of a tetraphenylporphyrin nickel (NiTPP) with and without two axial piperidine ligands are shown in the left panel of Figure 5. The calculations were done with the FEFF 8.0 program.⁽²³⁻²⁵⁾ It shows that we can use $L_{\alpha 1}$ and $L_{\alpha 2}$ of tungsten to probe the K edge of Ni in order to study this photochemical reaction. In this example, the patterns are drastically different between the complexed and dissociated NiTPP. We have to point out that although these main features of the calculated results resemble the real spectra, the position of the pre-edge peak corresponding to the $1s-4p$ ($3d$) transitions is obviously different from the one shown in the static measurements.⁽²²⁾ In order to truthfully reproduce these spectra, higher levels of calculations may be needed.⁽²⁶⁾

5. CONCLUSION

We have demonstrated the principle of USEXAS in which one can use characteristic x-ray radiation from a laser-driven electron x-ray source to study reaction dynamics in condensed phase. Our results show that it is possible to obtain absorption data in both near edge and the extended regions from which dynamic information can be inferred.

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REFERENCES

1. G. J. Cheng, F. Shan, A. Freyer and T. Guo, Compact 50-Hz terawatt Ti : sapphire laser for x-ray and nonlinear optical spectroscopy, *Applied Optics* **41** (24), 5148-5154 (2002).
2. C. Leblanc, G. Grillon, J. P. Chambaret, A. Migus and A. Antonetti, Compact and Efficient Multipass Ti-Sapphire System For Femtosecond Chirped-Pulse Amplification At the Terawatt Level, *Optics Letters* **18** (2), 140-142 (1993).
3. C. P. J. Barty, T. Guo, C. Leblanc, F. Raksi, C. Rosepetruck, J. Squier, K. R. Wilson, V. V. Yakovlev and K. Yamakawa, Generation of 18-Fs, Multiterawatt Pulses By Regenerative Pulse Shaping and Chirped-Pulse Amplification, *Optics Letters* **21** (9), 668-670 (1996).
4. T. Guo, C. Spielmann, B. C. Walker and C. P. J. Barty, Generation of hard x rays by ultrafast terawatt lasers, *Review of Scientific Instruments* **72** (1 PT1), 41-47 (2001).
5. C. Rischel, A. Rousse, I. Uschmann, P. A. Albouy, J. P. Geindre, P. Audebert, J. C. Gauthier, E. Forster, J. L. Martin *et al.*, Femtosecond time-resolved X-ray diffraction from laser-heated organic films, *Nature* **390** (6659), 490-492 (1997).
6. C. Rose-Petruck, R. Jimenez, T. Guo, A. Cavalleri, C. W. Siders, F. Raksi, J. A. Squier, B. C. Walker, K. R. Wilson *et al.*, Picosecond-milliangstrom lattice dynamics measured by ultrafast X-ray diffraction, *Nature* **398** (6725), 310-312 (1999).
7. M.H. Key and R.J. Hutcheon, Spectroscopy of Laser Produced Plasmas, *Adv. At. Mol. Opt. Phys.* **16**, 201 (1980).
8. A.A. Hauer and G.A. Kyrala, "Laser-Plasma X-ray Emission: Its Creation, Diagnosis, and Applications in Transient Diffraction," in *Time-Resolved Diffraction*, edited by J.R and Rentzepis Helliwell, P.M. (Clarendon Press; Oxford University Press, Oxford, New York, 1997), pp. 71-105.
9. J. D. Kmetec, C. L. Gordon, J. J. Macklin, B. E. Lemoff, G. S. Brown and S. E. Harris, MeV X-Ray Generation With a Femtosecond Laser, *Phys. Rev. Lett.* **68** (10), 1527-1530 (1992).

10. A. Rousse, P. Audebert, J. P. Geindre, F. Fallies, J. C. Gauthier, A. Mysyrowicz, G. Grillon and A. Antonetti, Efficient K Alpha X-Ray Source From Femtosecond Laser-Produced Plasmas, *Physical Review E* **50** (3), 2200-2207 (1994).
11. R. W. Schoenlein, S. Chattopadhyay, H. H. W. Chong, T. E. Glover, P. A. Heimann, C. V. Shank, A. A. Zholents and M. S. Zolotarev, Generation of femtosecond pulses of synchrotron radiation, *Science* **287** (5461), 2237-2240 (2000).
12. I. V. Tomov, D. A. Oulianov, P. L. Chen and P. M. Rentzepis, Ultrafast time-resolved transient structures of solids and liquids studied by means of X-ray diffraction and EXAFS, *J. Phys. Chem. B* **103** (34), 7081-7091 (1999).
13. J. Larsson, P. A. Heimann, A. M. Lindenberg, P. J. Schuck, P. H. Bucksbaum, R. W. Lee, H. A. Padmore, J. S. Wark and R. W. Falcone, Ultrafast structural changes measured by time-resolved X-ray diffraction, *Appl. Phys. A-Mat. Sci. & Proc.* **66** (6), 587-591 (1998).
14. T. Guo, Rose-Petruck, C., Jimenez, R., Raski, F., Squier, J., Walker, B.C., Wilson, K.R., Barty, C.P.J., "Picosecond-milliangstrom resolution dynamics by ultrafast X-ray diffraction," presented at the SPIE, San Diego, 1997 (unpublished).
15. A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, P. Balcou, E. Foster, J. P. Geindre *et al.*, Non-thermal melting in semiconductors measured at femtosecond resolution, *Nature* **410** (6824), 65-68 (2001).
16. D. C. Koningsberger and Roelof Prins, *X-ray absorption : principles, applications, techniques of EXAFS, SEXAFS, and XANES* (Wiley, New York, 1988).
17. F. L. H. Brown, K. R. Wilson and J. S. Cao, Ultrafast extended x-ray absorption fine structure (EXAFS) - theoretical considerations, *J. Chem. Phys.* **111** (14), 6238-6246 (1999).
18. G. Cheng and T. Guo, Surface segregation in Ni/Co bimetallic nanoparticles produced in single-walled carbon nanotube synthesis, *J. Phys. Chem. B* **106** (23), 5833-5839 (2002).
19. G. Cheng, F. Shan, A. Freyer and T. Guo, "Ultrafast X-ray Absorption Spectroscopy using Laser Driven Electron X-ray Sources (LEXS)," presented at the Applications of X rays Generated from Lasers and Other Bright Sources II, San Diego, 2001 (unpublished).
20. F. Shan, J.D. Carter and T. Guo, *J. Chem. Phys.* **to be submitted** (2004).
21. A. Thompson *et al.*, *X-ray Data Booklet*, Rev.2 ed. (LBNL, Berkeley, CA, 2001).
22. L. X. Chen, W. J. H. Jager, G. Jennings, D. J. Gosztola, A. Munkholm and J. P. Hessler, Capturing a photoexcited molecular structure through time-domain X-ray absorption fine structure, *Science* **292** (5515), 262-264 (2001).
23. J. J. Rehr, A. Ankudinov and S. I. Zabinsky, New developments in NEXAFS/EXAFS theory, *Catalysis Today* **39** (4), 263-269 (1998).
24. J. J. Rehr, Multiple-Scattering Approach to Surface Exafs - Theory Versus Experiment, *Surface Review and Letters* **2** (1), 63-69 (1995).
25. A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure, *Phys. Rev. B-Cond. Mat* **58** (12), 7565-7576 (1998).
26. Y. Luo, H. Agren, M. Keil, R. Friedlein and W. R. Salaneck, A theoretical investigation of the near-edge X-ray absorption spectrum of hexa-peri-hexabenzocoronene, *Chem. Phys. Lett.* **337** (1-3), 176-180 (2001).