Initial metal-metal bond breakage detected by fs X-ray scattering in the photolysis of Ru$_3$(CO)$_{12}$ in cyclohexane at 400 nm

Using femtosecond resolution X-ray solution scattering at a free electron laser we were able to directly observe metal-metal bond cleavage upon photolysis at 400 nm of Ru$_3$(CO)$_{12}$, a prototype for the photochemistry of transition metal carbonyls. This leads to the known single intermediate Ru$_3$(CO)$_{11}$(μ-CO)$^*$, with a bridging ligand (μCO) and where the asterisk indicates an open Ru$_3$-ring. This loses a CO ligand on a picosecond time scale yielding a newly observed triple bridge intermediate, Ru$_3$(CO)$_9$(μ-CO)$_2$$^*$. This loses another CO ligand to form the previously observed Ru$_3$(CO)$_{10}$ which returns to Ru$_3$(CO)$_{12}$ via the known single-bridge Ru$_3$(CO)$_{10}$(μ-CO). These results indicate that contrary to long standing hypotheses, metal-metal bond breakage is the only chemical reaction immediately following the photolysis of Ru$_3$(CO)$_{12}$ at 400 nm. Combined with previous picosecond resolution X-ray scattering data and time resolved infrared spectroscopy these results yield a new mechanism for the photolysis of Ru$_3$(CO)$_{12}$.
Theoretical Evidence of Solvent-Mediated Excited-State Dynamics in a Functionalized Iron Sensitizer

The solvent-mediated excited-state dynamics of the COOH-functionalized Fe-carbene photosensitizer \([\text{Fe(bmicp)}_2]^{2+}\) (bmicp = 2,6-bis-(3-methyl-imidazole-1-ylidene)-4-carboxy-pyridine) is studied by time-dependent density functional theory, as well as classical and quantum dynamics simulations. We demonstrate the crucial role of the polar acetonitrile solvent in stabilizing the metal-to-ligand charge transfer (MLCT) states of the investigated molecule using the conductor polarizable continuum model. This leads to dynamics that avoid sub-ps back electron transfer to the metal and an exceptionally long-lived 1MLCT state that does not undergo sub-ps 1MLCT \(\rightarrow\) 3MLCT intersystem crossing as it is energetically isolated. We identify two components of the excited-state solvent reorganization process: an initial rotation (∼300 fs) and diffusional dynamics within the local cage surrounding the rotated solvent molecule (∼2 ps). Finally, it is found that the relaxation of the solvent only slightly affects the excited-state population dynamics of \([\text{Fe(bmicp)}_2]^{2+}\).

General information
State: Accepted/In press
Organisations: Department of Chemistry, Neutrons and X-rays for Materials Physics, Department of Physics
Number of pages: 10
Publication date: 2019
Peer-reviewed: Yes
Anisotropy enhanced X-ray scattering from solvated transition metal complexes

Time-resolved X-ray scattering patterns from photoexcited molecules in solution are in many cases anisotropic at the ultrafast time scales accessible at X-ray free-electron lasers (XFELs). This anisotropy arises from the interaction of a linearly polarized UV-Vis pump laser pulse with the sample, which induces anisotropic structural changes that can be captured by femtosecond X-ray pulses. In this work, a method for quantitative analysis of the anisotropic scattering signal arising from an ensemble of molecules is described, and it is demonstrated how its use can enhance the structural sensitivity of the time-resolved X-ray scattering experiment. This method is applied on time-resolved X-ray scattering patterns measured upon photoexcitation of a solvated di-platinum complex at an XFEL, and the key parameters involved are explored. It is shown that a combined analysis of the anisotropic and isotropic difference scattering signals in this experiment allows a more precise determination of the main photoinduced structural change in the solute, i.e. the change in Pt-Pt bond length, and yields more information on the excitation channels than the analysis of the isotropic scattering only. Finally, it is discussed how the anisotropic transient response of the solvent can enable the determination of key experimental parameters such as the instrument response function.

General information

State: Published
Organisations: Department of Physics, Neutrons and X-rays for Materials Physics, Department of Chemistry, Department of Electric Power Engineering, University of Iceland, SLAC National Accelerator Laboratory, Technical University of Denmark
Pages: 306-315
Publication date: 2018
Peer-reviewed: Yes

Publication information

Journal: Journal of Synchrotron Radiation
Volume: 25
Issue number: 2
ISSN (Print): 0909-0495
Ratings:
BFI (2019): BFI-level 1
Web of Science (2019): Indexed yes
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 3.12 SJR 1.65 SNIP 1.431
Web of Science (2017): Impact factor 3.232
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.86 SJR 1.521 SNIP 1.491
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 2.45 SJR 1.146 SNIP 1.301
Web of Science (2015): Impact factor 1.877
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 2.58 SJR 1.317 SNIP 1.477
Solvent control of charge transfer excited state relaxation pathways in [Fe(2,2’-bipyridine)(CN)4]2-

The excited state dynamics of solvated [Fe(bpy)(CN)4]2-, where bpy = 2,2'-bipyridine, show significant sensitivity to the solvent Lewis acidity. Using a combination of optical absorption and X-ray emission transient spectroscopies, we have previously shown that the metal to ligand charge transfer (MLCT) excited state of [Fe(bpy)(CN)4]2- has a 19 picosecond lifetime and no discernable contribution from metal centered (MC) states in weak Lewis acid solvents, such as dimethyl sulfoxide and acetonitrile. 1,2 In the present work, we use the same combination of spectroscopic techniques to measure the MLCT excited state relaxation dynamics of [Fe(bpy)(CN)4]2- in water, a strong Lewis acid solvent. The charge-transfer excited state is now found to decay in less than 100 femtoseconds, forming a quasi-stable metal centered excited state with a 13 picosecond lifetime. We find that this MC excited state has triplet (3MC) character, unlike other reported six-coordinate Fe(II)-centered coordination compounds, which form MC quintet (5MC) states. The solvent dependent changes in excited state non-radiative relaxation for [Fe(bpy)(CN)4]2- allows us to infer the influence of the solvent on the electronic
structure of the complex. Furthermore, the robust characterization of the dynamics and optical spectral signatures of the isolated $^{3}$MC intermediate provides a strong foundation for identifying $^{3}$MC intermediates in the electronic excited state relaxation mechanisms of similar Fe-centered systems being developed for solar applications.

**General information**

State: Published

Organisations: Department of Physics, Neutrons and X-rays for Materials Physics, SLAC National Accelerator Laboratory, Stanford University, Lund University, Hungarian Academy of Sciences, Deutsches Elektronen-Synchrotron


Pages: 4238-4249
Publication date: 2018
Peer-reviewed: Yes

**Publication information**

Journal: Physical Chemistry Chemical Physics
Volume: 20
Issue number: 6
ISSN (Print): 1463-9076

Ratings:
- BFI (2019): BFI-level 2
- Web of Science (2019): Indexed yes
- BFI (2018): BFI-level 2
- Web of Science (2018): Indexed yes
- BFI (2017): BFI-level 2
- Scopus rating (2017): CiteScore 4.04 SJR 1.686 SNIP 1.089
- Web of Science (2017): Impact factor 3.906
- Web of Science (2017): Indexed yes
- BFI (2016): BFI-level 2
- Scopus rating (2016): CiteScore 4.06 SJR 1.685 SNIP 1.113
- Web of Science (2016): Impact factor 4.123
- Web of Science (2016): Indexed yes
- BFI (2015): BFI-level 2
- Scopus rating (2015): CiteScore 4.45 SJR 1.725 SNIP 1.205
- Web of Science (2015): Indexed yes
- BFI (2014): BFI-level 2
- Scopus rating (2014): CiteScore 4.29 SJR 1.771 SNIP 1.239
- Web of Science (2014): Impact factor 4.493
- Web of Science (2014): Indexed yes
- BFI (2013): BFI-level 2
- Scopus rating (2013): CiteScore 4.05 SJR 1.72 SNIP 1.207
- Web of Science (2013): Impact factor 4.198
- ISI indexed (2013): ISI indexed yes
- Web of Science (2013): Indexed yes
- BFI (2012): BFI-level 2
- Scopus rating (2012): CiteScore 3.67 SJR 1.921 SNIP 1.177
- Web of Science (2012): Impact factor 3.829
- ISI indexed (2012): ISI indexed yes
- Web of Science (2012): Indexed yes
- BFI (2011): BFI-level 2
- Scopus rating (2011): CiteScore 3.6 SJR 1.707 SNIP 1.19
- Web of Science (2011): Impact factor 3.573
- ISI indexed (2011): ISI indexed yes
- Web of Science (2011): Indexed yes
Tracking the picosecond deactivation dynamics of a photoexcited iron carbene complex by time-resolved X-ray scattering

Recent years have seen the development of new iron-centered N-heterocyclic carbene (NHC) complexes for solar energy applications. Compared to typical ligand systems, the NHC ligands provide Fe complexes with longer-lived metal-to-ligand charge transfer (MLCT) states. This increased lifetime is ascribed to strong ligand field splitting provided by the NHC ligands that raises the energy levels of the metal centered (MC) states and therefore reduces the deactivation efficiency of MLCT states. Among currently known NHC systems, [Fe(btbip)2]^2+ (btbip = 2,6-bis(3-tert-butyl-imidazol-1-ylidene)pyridine) is a unique complex as it exhibits a short-lived MC state with a lifetime on the scale of a few hundreds of picoseconds. Hence, this complex allows for a detailed investigation, using 100 ps X-ray pulses from a synchrotron, of strong ligand field effects on the intermediate MC state in an NHC complex. Here, we use time-resolved wide angle X-ray scattering (TRWAXS) aided by density functional theory (DFT) to investigate the molecular structure, energetics and lifetime of the high-energy MC state in the Fe-NHC complex [Fe(btbip)2]^2+ after excitation to the MLCT manifold. We identify it as a 260 ps metal-centered quintet (5MC) state, and we refine the molecular structure of the excited-state complex verifying the DFT results. Using information about the hydrodynamic state of the solvent, we also determine, for the first time, the energy of the 5MC state as 0.75 + 0.15 eV. Our results demonstrate that due to the increased ligand field strength caused by NHC ligands, upon transition from the ground state to the 5MC state, the metal to ligand bonds extend by unusually large values: by 0.29 angstrom in the axial and 0.21 angstrom in the equatorial direction. These results imply that the transition in the photochemical properties from typical Fe complexes to novel NHC compounds is manifested not only in the destabilization of the MC states, but also in structural distortion of these states.

General information
State: Published
Organisations: Neutrons and X-rays for Materials Physics, Department of Physics, European Synchrotron Radiation Facility, Lund University, European XFEL
Femtosecond X-Ray Scattering Study of Ultrafast Photoinduced Structural Dynamics in Solvated [Co(terpy)₂]²⁺

We study the structural dynamics of photoexcited [Co(terpy)₂]²⁺ in an aqueous solution with ultrafast x-ray diffuse scattering experiments conducted at the Linac Coherent Light Source. Through direct comparisons with density functional theory calculations, our analysis shows that the photoexcitation event leads to elongation of the Co-N bonds, followed by coherent Co-N bond length oscillations arising from the impulsive excitation of a vibrational mode dominated by the symmetrical stretch of all six Co-N bonds. This mode has a period of 0.33 ps and decays on a subpicosecond time scale. We find that the equilibrium bond-elongated structure of the high spin state is established on a single-picosecond time scale and that this state has a lifetime of ~7 ps.

General information
State: Published
Organisations: Department of Physics, Neutrons and X-rays for Materials Physics, Theoretical Atomic-scale Physics, Department of Chemistry, Lund University
Number of pages: 6
Publication date: 2016
Peer-reviewed: Yes

Publication information
Journal: Physical Review Letters
Volume: 117
Issue number: 1
Article number: 013002
ISSN (Print): 0031-9007
Ratings:
BFI (2019): BFI-level 2
Web of Science (2019): Indexed yes
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 7.58 SJR 3.622 SNIP 2.464
Web of Science (2017): Impact factor 8.839
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 6.33 SJR 4.196 SNIP 2.61
Web of Science (2016): Impact factor 8.462
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 5.76 SJR 4.656 SNIP 2.538
Disentangling detector data in XFEL studies of temporally resolved solution state chemistry
With the arrival of X-ray Free Electron Lasers (XFELs), 2D area detectors with a large dynamic range for detection of hard X-rays with fast readout rates are required for many types of experiments. Extracting the desired information from these detectors has been challenging due to unpredicted fluctuations in the measured images. For techniques such as time-resolved X-ray Diffuse Scattering (XDS), small differences in signal intensity are the starting point for analysis. Fluctuations in the total detected signal remain in the differences under investigation, obfuscating the signal. To correct such artefacts, Singular Value Decomposition (SVD) can be used to identify and characterize the observed detector fluctuations and assist in assigning some of them to variations in physical parameters such as X-ray energy and X-ray intensity. This paper presents a methodology for robustly identifying, separating and correcting fluctuations on area detectors based on XFEL beam characteristics, to enable the study of temporally resolved solution state chemistry on the femtosecond timescale.
On the calculation of x-ray scattering signals from pairwise radial distribution functions

We derive a formulation for evaluating (time-resolved) x-ray scattering signals of solvated chemical systems, based on pairwise radial distribution functions, with the aim of this formulation to accompany molecular dynamics simulations. The derivation is described in detail to eliminate any possible ambiguities, and the result includes a modification to the atom-type formulation which to our knowledge is previously unaccounted for. The formulation is numerically implemented and validated.

General information
State: Published
Organisations: Center for Atomic-scale Materials Design, Department of Chemistry, Department of Physics, Neutrons and X-rays for Materials Physics, Physical and Biophysical Chemistry
Contributors: Dohn, A. O., Biasin, E., Haldrup, K., Nielsen, M. M., Henriksen, N. E., Møller, K. B.
Number of pages: 9