Anti-Stokes resonant x-ray Raman scattering for atom specific and excited state selective dynamics

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Abstract

Ultrafast electronic and structural dynamics of matter govern rate and selectivity of chemical reactions, as well as phase transitions and efficient switching in functional materials. Since x-rays determine electronic and structural properties with elemental, chemical, orbital and magnetic selectivity, short pulse x-ray sources have become central enablers of ultrafast science. Despite of these strengths, ultrafast x-rays have been poor at picking up excited state moieties from the unexcited ones. With time-resolved anti-Stokes resonant x-ray Raman scattering (AS-RXRS) performed at the LCLS, and \textit{ab initio} theory we establish background free excited state selectivity in addition to the elemental, chemical, orbital and magnetic selectivity of x-rays. This unparalleled selectivity extracts low concentration excited state species along the pathway of photo induced ligand exchange of Fe(CO)5 in ethanol. Conceptually a full theoretical treatment of all accessible insights to excited state dynamics with AS-RXRS with transform-limited x-ray pulses is given—which will be covered experimentally by upcoming transform-limited x-ray sources.

With the rapid evolution of sub-picosecond and femtosecond x-ray sources and particularly with the emergence x-ray free-electron lasers, first steps to join the unique electronic structure information of x-ray spectroscopy with the ultrafast time scale of dynamics in matter have been taken [1–8]. Often though, time resolved x-ray spectroscopy at these dilute transient species with x-ray absorption, x-ray fluorescence or electron spectroscopy suffer often from the difficult separation between the overlapping spectral signatures of the dilute excited state species and the ground state. To reach improved chemical selectivity with x-ray lasers nonlinear and
multidimensional approaches have been explored both theoretically and experimentally [9–15]. In this work, we show how anti-Stokes resonant x-ray Raman scattering (AS-RXRS) adds unique excited state selectivity to already highly selective resonant inelastic x-ray scattering (RIXS) technique. In recent years, RIXS as a resonantly driven Stokes x-ray Raman process has gradually reached relevant energy scales [16–18] to map out magnetic [19], charge [20], orbital [21] and structural excitations [22, 23] as well as complex potential energy surfaces [24, 25] of functional materials and chemical processes. Additionally, stimulated x-ray Raman scattering was recently used to enhance the RIXS signals [26, 27].

To establish AS-RXRS we use the photochemical pathway of the photoinduced ligand exchange reaction of Fe(CO)₅ in ethanol solution (figure 1(A)) and conduct AS-RXRS at the Fe L₃-edge of the electronically excited Fe(CO)₅ and Fe(CO)₅ species transiently present along the reaction pathway toward the ligand substituted Fe(CO)₅EtOH (figure 1(B)) [28, 29]. This dynamic pathway has been introduced for the gas phase by Trushin et al in [30] and modified for ethanol solution by the mechanism of ultrafast ligand addition and spin crossover by previous work of the authors [28, 29]. Cascading dynamics of electronically excited states in Fe(CO)₅ is initiated by resonant absorption of a 266 nm (4.66 eV) photon. The initial photo-absorption creates a metal-to-ligand charge-transfer (MLCT) 3E state which due to Jahn–Teller-like nuclear dynamics converts through possibly multiple internal conversions to a ligand field (LF) 1E′ state with a time constant of 21 fs [30]. The conversion therefore includes a relaxation of an electron from delocalized 2π⁎ orbital to localized dₓ² orbital (electron back-transfer). Since dₓ² is strongly σ-antibonding with respect to the Fe-CO bond, a Jahn–Teller-like motion on the 1E′(LF) surface leads to a transition state (15 fs) which is followed by a dissociation of a single CO ligand and the creation of Fe(CO)₄ in an excited 1B₂(LF) state (30 fs) [30]. This electronically excited state evolution we summarize as 1E′(MLCT) → 1E′(LF) and 1E′(LF) → 1B₂(LF), with 20 fs and 45 fs time constants, respectively (figure 1(B)). Later, ultrafast ligand addition, spin crossover and geminate recombination finally leads to a branching from the vibrationally hot Fe(CO)₄ Å that is in the electronic ground state to the ground state ligand substituted complex Fe(CO)₅EtOH and the picosecond lived high spin Fe(CO)₅ 3B₂ state [30]. The electronically excited states involved 1E′(MLCT), 1E′(LF) and 1B₂(LF) can lead in resonant x-ray Raman Scattering to the emission of x-rays photons with an energy higher than the incident x-ray photon energy (hυ_{X_{out}} > hυ_{X_{in}}), which is the anti-Stokes Raman signature in this x-ray analog to optical time-resolved resonant Raman spectroscopy. As depicted in figure 1(C) this AS-RXRS energy transfer/anti-Stokes shift corresponds to the valence electronic excitation energies.

Figure 1. Photo-induced ligand substitution of Fe(CO)₅ in ethanol solution into Fe(CO)₅EtOH and its relation to AS-RXRS. (A) Depiction of ligand substitution and AS-RXRS at the Fe L₃ edge. (B) Reaction pathway involving the electronic ground states of Fe(CO)₅, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A′, A'
Results

In figure 2 we show on the left side panels the electronic orbital structure of ground state Fe(CO)$_5$ (figure 2(A)) and how the Stokes resonant x-ray Raman scattering (also commonly denoted as resonant inelastic x-ray scattering, RIXS) leads in the schematic representation of the inelastic x-ray scattering plane (figure 2(C)) to a participator channel with zero energy transfer, and to Stokes energy transfer (loss) due to the creation of final state electron–hole pairs. In figure 2(E) the RIXS map of the Fe(CO)$_5$ ground state calculated with ab initio restricted active space self-consistent field (RASSCF) method [31] is shown (see methods for further details). On
the right-hand side panels (B) and (D) of figure 2, we describe how in an one-electron orbital picture the creation of an initial electronic MLCT excitation through optical absorption leads to the opening of a lower energy scattering resonance and the occurrence of fully separated AS-RXRS spectral signatures. Different from the ground state, the optically excited Fe(CO)$_3$ 1E'(MLCT) state has a valence vacancy in the d$_z^2$ orbital. Thus a new energetically lower x-ray scattering resonance is opened up, depicted in figure 2(D). Resonant x-ray Raman Scattering through this excited state resonance occurs at a $h\nu_{exc}$-red-shifted core-level resonance energy and leads for all electron–hole pair final states to the appearance of inelastic scattering features with $h\nu_{exc}$-blue-shifted emission energies in relation to the ground state situation. This is the signature of AS-RXRS. The Resonant x-ray Raman Scattering planes calculated using the RASSCF method in the ground state and in the 1E'(MLCT) excited state in figures 2(E) and (F) confirm the conceptual reasoning based on the simplified one-electron orbitals. Therefore the AS-RXRS spectral features are a result of excitation to the d$_z^2$ vacancy that is followed by a decay of the excited electrons at the 2$\pi^*$ orbital. The most intense AS-RXRS peak in figure 2(F) is at $-5\mathrm{eV}$ energy transfer which corresponds to scattering to the 1A$_1$ ground state. Dipole selection rules apply to all the involved transitions (pump and probe) and we note that in case of molecules with inversion symmetry, anti-Stokes scattering from optically populated state to the ground state is dipole forbidden. This is not the case for Fe(CO)$_3$, which belongs to the D$_{3h}$ point group symmetry and thus has no inversion center.

In figure 3 we show all AS-RXRS maps of the excited states along the Fe(CO)$_3$ photodissociation pathway. The projections through the scattering planes (white dashed regions) in the AS-RXRS region yield the computed AS-RXRS matching the experimental ones. In particular, we can define spectral regions R1, R2, R3 (black solid regions) that detect background-free the AS-RXRS features of electronically excited states 1E'(MLCT) Fe(CO)$_3$, 1E'(LF) Fe(CO)$_3$ and 1B$_2$(LF) Fe(CO)$_3$, respectively. In addition (R4) picks up the 3B$_2$(LF) Fe(CO)$_3$ electronic ground state reached after CO detachment. Transient occupation of these states is shown on the right-hand side panels of figure 3. We note that computational treatment of AS-RXRS from different excited molecules have been done before by Tanaka et al and Pandey et al[32, 33].

In figure 4 direct comparison of experimental and simulated Fe L$_{3,2}$-edge AS-RXRS signatures along the Fe(CO)$_3$ to Fe(CO)$_3$EtOH ligand substitution pathway is shown. In the panel (A) of figure 4 the resonant x-ray scattering difference map is shown in the center. Along the axis of incident photon energy we observe the opening of the red-shifted x-ray scattering resonance due to the optically created initial 1E'(MLCT) state at $-4.6\mathrm{eV}$ excitation energy equal to the pump photon energy (266 nm). Within this spectral region along the emission energy axis the occurrence of blue-shifted anti-Stokes features occurs. The AS-RXRS region R3 shows the transience of the convoluted temporal resolution and the excited state dynamics. The anti-Stokes intensity disappears after 400 fs, with a deconvoluted exponential time constant of $\sim 100\mathrm{fs}$, visible from the delay scans in figure 4(A). Region R4 of the 1B$_2$ Fe(CO)$_3$ photoproduct retains significant intensity.

To fully describe the experimental observables (figure 4(A)) through the photochemical pathway of figure 1(B) [28–30], we simulate the observed AS-RXRS features using the RASSCF calculations for all involved excited states from figure 3 and the kinetic rate model of the photochemical pathway (figure 1(B)), taking into account the experimental time resolution of 300 fs and the experimental spectral broadening contributions (figure 4(B), and methods). At these conditions the AS-RXRS feature is dominated by the electronically excited 1B$_2$(LF) state of Fe(CO)$_3$ in region R3 (figure 3(C)). The 1E'(MLCT) and 1E'(LF) states (with 20 fs and 45 fs lifetimes, respectively) are less pronounced (inset in the simulated RIXS spectrum in figure 4(B)). The 1B$_2$(LF) Fe(CO)$_3$ state correlates with the 1E'(LF) Fe(CO)$_3$ state, however it has significantly lower energy due to strong structural relaxation which has taken place (i.e. CO dissociation); based on the RASSCF calculation, the 1E'(LF) state is $4.6\mathrm{eV}$ above the Fe(CO)$_3$ ground state, whereas the relaxed 1B$_2$(LF) state has only $\sim 1\mathrm{eV}$ higher energy compared to the Fe(CO)$_3$ 1A$_1$ state. Thus this energy relaxation leads to the AS-RXRS feature with a smaller blue shift in comparison to the initial optical excitation energy of $h\nu_{exc} = 4.66\mathrm{eV}$. Simulation of the AS-RXRS feature at 706–707 eV incident photon energy region in figure 4(B) reproduces remarkably well the experimental spectral shape (note that RASSCF calculations at the 2$\pi^*$ core resonance at 710–714 eV are less accurate). The lifetime of 1B$_2$(LF) state is $\sim 100\mathrm{fs}$ and it relaxes via two parallel process to the 1A$_1$ ground state of four-coordinated Fe(CO)$_3$L or to the 1B$_2$, ground state of five-coordinated Fe(CO)$_4$L ($L = \text{EtOH, CO}$) [21]. This results in disappearance of the anti-Stokes scattering feature (region R3), whereas considerably intensity close to elastic peak at 706–707 eV (region R4) remains due to the 1B$_2$(LF) Fe(CO)$_3$ state (figure 3(D)).

**Discussion**

We can now demonstrate in figure 5 the full potential of AS-RXRS with transform–limited Gaussian x-ray pulses ($\Delta E \Delta t = 0.44\mathrm{h}$) from upcoming x-ray lasers [34, 35]. Three prototypical scenarios focusing on the initial electron back-transfer between the Fe(CO)$_3$ 1E'(MLCT) and 1E'(LF) states and subsequent CO removal during 1E'(LF) to 1B$_2$(LF) inter conversion are presented. As defined in figure 3, anti-Stokes features of the 1E'(MLCT),
1E'(LF) and 1B2(LF) states are picked up within R1, R2 and R3, located at −5 eV, −4.6 eV and −1 eV energy transfer, respectively. AS-RXRS preserves the bandwidth $\Delta E$ of the scattered radiation at linear dispersion with an upper limit given by the natural core-hole lifetime broadening $\Gamma$ (0.3 eV at the Fe $L_3$-edge) reflecting the Fe $L_3$-edge 2.2 fs natural core-hole lifetime. We give the overall temporal resolution in the simulation as the convolution of probe and pump pulses at delay $t$ (assumed equal in duration). With different pulse length $\Delta t$, both the temporal resolution and the chemical selectivity can be varied and finest details of the dynamics and potential energy surfaces of excited states can be extracted background free. Column A of figure 5 shows highest temporal selectivity with a pulse duration of $\Delta t = 1$ fs that separates the 1E'(MLCT) and 1E'(LF) states in time, but with $\Delta E = 2.0$ eV incident bandwidth at the cost of no spectral selectivity. However, the features from the 1E'(MLCT) and 1E'(LF) states can still be well distinguished since increasing the bandwidth beyond the core-hole lifetime broadening does not result in further broadening of the spectra. Column B of figure 5 shows optimized chemical selectivity and temporal resolution through a transform limited pulse with $\Delta E = 0.2$ eV and a pulse

![Diagram](image-url)
duration of $\Delta t = 10$ fs. This yields distinction both energetically and temporally and separates AS-RXRS features of the $1E'$ (MLCT), $1E'$ (LF) and $1B_2$ (LF) states. Column C of figure 5 shows how sub-natural linewidth resolution maps out the potential energy surfaces [22, 25, 36] of the $1E'$ (MLCT), $1E'$ (LF) excited states individually for transform limited pulses with $\Delta E = 0.02$ eV and pulse duration of $\Delta t = 100$ fs. Although no direct temporal separation occurs, the chemical shift between the x-ray scattering resonances of the different $1E'$ (MLCT), $1E'$ (LF) excited states separates them, thus allowing to map the potential energy surface of the excited states undergoing rapid photochemical dynamics.

**Methods**

**Computational details**

Theoretical x-ray spectra were derived from RASSCF calculations [37] using the MOLCAS-7 software [38]. For further details see [28, 29]. The geometries were optimized with the CASPT2 method [39] and the TZVP basis set [40] for all atoms. The active space contained 12 electrons in 12 orbitals. Some of the geometries were optimized with density functional theory using the PBE functional [41] and the TZVP basis set.

Following experimental factors contribute to the spectral linewidth in the experiment and are taken into account in the simulation of the experiment: the 0.3 eV core-hole lifetime broadening, 0.5 eV incident x-ray bandwidth, 1 eV spectrometer resolution and the 0.5 eV due to inhomogeneous broadening from solvent environment and vibrational effects (all values FWHM). RIXS spectra were simulated using the Kramers–
Heisenberg formula. Spectra were calculated for an ensemble of randomly oriented molecules excited by linearly polarized light and detected in the plane of polarization. Interference effects were excluded.

**Experimental details**

Experiment was performed at the linac coherent light source (LCLS) soft x-ray materials science (SXR) instrument [42, 43] with the liquid jet endstation [44]. The 1 mol l⁻¹ Fe(CO)₅ ethanol solution was photo-excited at 266 nm (4.66 eV). The pump-laser pulse duration amounted to 100 fs (FWHM) and the pulse energy was estimated to ∼5 μJ. With a pump-laser spot size of 100 × 400 μm², this corresponded to a peak fluence of ∼1.25 × 10¹¹ W cm⁻². We found no evidence for multi-photon processes at this fluence of the pump laser.

Fe L₃-RIXS intensities were measured by scanning the incident photon energy from 703 to 715 eV. The resolution in the RIXS measurements along the incident-photon energy axis is defined by the excitation bandwidth. This amounted here to 0.5 eV (FWHM) and was determined by the slit size of 150 μm of the SXR monochromator. Incident flux was measured on a shot-by-shot basis using intensity monitor installed after the monochromator [45].

Figure 5. AS-RXRS features computed with Gaussian transform limited x-ray pulses exploring three complementary scenarios at the Fe L₃-edge and at time delays t demonstrate the ability to resolve excited state selective ultrafast internal conversion between ¹E′ (MLCT) and ¹E′ (LF) states (electron back-transfer) and subsequent CO removal during ¹E′ (LF) to ¹B₂ (LF) inter conversion (¹E′ (MLCT), ¹E′ (LF), ¹B₂ (LF) AS-RXRS regions within R1, R2, R3 respectively). The gray areas in the top panels spans ΔE₅t in relation to the dynamics and energies involved in the initial electron back-transfer between the Fe(CO)₅ ¹E′ (MLCT) and ¹E′ (LF) states. (A) Highest temporal selectivity with Δt = 1 fs and ΔE = 2.0 eV. (B) Temporal and spectral selectivity with ΔE = 0.2 eV and Δt = 10 fs. (C) Potential energy surface mapping with sub-natural linewidth energy resolution ΔE = 0.02 eV and Δt = 100 fs.
Competing financial interests

The authors declare no competing financial interests.

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Author contributions

The manuscript was written by KK and AF with input from all co-authors. IJ and MO carried out the RASSCF calculations. KK, IR, SS, WQ, MB, SG, MS, DN, WZ, RWH, KJG, WFS, JYT, BK, FH, ST, PW and AF carried out the experiment.

Additional information

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