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**Time-Resolved Femtosecond Stimulated Raman Spectra and
DFT Anharmonic Vibrational Analysis of an Electronically
Excited Rhenium Photosensitizer**

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Time-Resolved Femtosecond Stimulated Raman Spectra and DFT Anharmonic Vibrational Analysis of an Electronically Excited Rhenium Photosensitizer

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Abstract

Time-resolved femtosecond stimulated Raman spectra (FSRS) of a prototypical organometallic photosensitizer/photocatalyst $\text{ReCl}(\text{CO})_3(2,2'\text{-bipyridine})$ were measured in a broad spectral range $\sim 40\text{--}2000$ (4000) cm^{-1} at time delays from 40 fs to 4 ns after 400 nm excitation of the lowest allowed electronic transition. Theoretical ground- and excited-state Raman spectra were obtained by anharmonic vibrational analysis using second-order vibrational perturbation theory on vibrations calculated by harmonic approximation at DFT-optimized structures. A good match with anharmonically calculated vibrational frequencies allowed for assigning experimental Raman features to particular vibrations. Observed frequency shifts upon excitation ($\nu(\text{ReCl})$ and $\nu(\text{CC inter-ring})$ vibrations upwards; $\nu(\text{CC, CN})$ and $\nu(\text{Re-C})$ downwards) are consistent with the bonding/antibonding characters of HOMO and LUMO involved in the excitation and support the delocalized formulation of the lowest triplet state as $\text{ReCl}(\text{CO})_3 \rightarrow \text{bpy}$ charge-transfer. FSRS

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3 spectra show a mode-specific temporal evolution, providing insight into the intersystem
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5 crossing (ISC) mechanism and subsequent relaxation. Most of the Raman features are present
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7 at ~ 40 fs and exhibit small shifts and intensity changes with time. The $1450\text{--}1600\text{ cm}^{-1}$ group of
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9 bands due to CC, CN, and CC(inter-ring) stretching vibrations undergoes extensive restructuring
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11 between 40 and ~ 150 fs, followed by frequency upshifts and a biexponential (0.38, 21 ps) area
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13 growth, indicating progressing charge separation in the course of the formation and relaxation
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15 of the lowest triplet state. Early (40–150 fs) restructuring was also observed in the low-
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17 frequency range for $\nu(\text{Re-Cl})$ and $\delta(\text{Re-C-O})$ vibrations that are presumably activated by ISC.
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19 FSRs experimental innovations employed to measure low- and high- energy Raman features
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21 simultaneously are described and discussed in detail.
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30 ■ INTRODUCTION

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32 Time-resolved vibrational spectroscopic methods are excellent techniques to
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34 characterize electronically excited states, as well as products and intermediates of
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36 photochemical reactions. Time-resolved infrared (TRIR)^{1,2} and Raman^{3,4,5,6,7} experiments
37
38 provide structural and dynamical information through temporal evolution of spectral patterns,
39
40 band shapes, and intensities. Comparing ground- and excited-state spectra allow us to
41
42 understand structural changes and electron-density redistribution upon excitation. The time
43
44 evolution of IR and Raman band positions and shapes report on relaxation processes while
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46 time-dependent band intensities (areas) shed light on excited-state decay and reactivity.
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52 To extract maximum information from vibrational spectroscopic experiments, we need
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54 to measure over spectral and temporal ranges as broad as possible and the spectral features
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3 must be correctly assigned to corresponding vibrations. TRIR spectra are usually reported at
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5 frequencies higher than $\sim 1100\text{ cm}^{-1}$, often focusing on strong IR chromophores (inorganic
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7 carbonyls, cyanides, isocyanides, SCN^- , $-\text{C}\equiv\text{C}-$, etc.) that give rise to well-separated bands
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9 between 1800 and 2300 cm^{-1} . Important results were also obtained in the region aromatic CC
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11 vibrations² which, however, is more crowded, complicating the spectral assignment. Time-
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13 resolved femtosecond stimulated Raman spectroscopy (TR-FSRS) is complementary to TRIR and
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15 could be more selective for particular chromophores owing to (pre)resonance enhancement.
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17 Although the low-frequency range ($\sim 40\text{--}800\text{ cm}^{-1}$) could be very informative, most FSRS studies
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19 report spectra above $\sim 800\text{ cm}^{-1}$, presumably due to technical difficulties in generating the
20
21 probing white-light continuum close to the Raman pump wavelength.
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28 Assignment of intense high-frequency vibrational bands can be done empirically in
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30 combination with symmetry arguments, but this approach often fails in fingerprint and,
31
32 especially, low-frequency regions. Moreover, molecular vibrations are substantially more
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34 delocalized over different bonds and more strongly coupled than can be captured by empirical
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36 assignments. Contemporary DFT software packages routinely perform vibrational analysis by
37
38 treating molecular vibrations as harmonic oscillators. Such calculations predict main spectral
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40 features and corresponding normal coordinates. However, the quantitative match between
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42 calculated and experimental frequencies often is not satisfactory, with accuracy decreasing at
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44 lower frequencies. Multiplicative correction factors, which depend on the basis set and the
45
46 functional, are often used. The harmonic approximation misses overtones and combination
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48 bands that contribute to spectral patterns and affect band shapes. It predicts equal energy
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50 spacing between vibrational levels and neglects many vibrational couplings, and is thus
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3 unsuitable for interpretation of diagonal and off-diagonal anharmonicities and cross-peaks in 2-
4 dimensional IR spectra.^{8,9} Anharmonic vibrational calculations overcome these problems.
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6 Computational techniques based on second-order vibrational perturbation theory (VPT2)
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8 suitable for medium-size molecular systems have been implemented only recently and were
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10 found to considerably improve the match between theory and experiment and to enable
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12 assignments of elusive spectral features.^{10,11,12,13,14}
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18 We report time-resolved FSRS of ground- and lowest electronic excited states of *fac*-
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20 $\text{ReCl}(\text{CO})_3(\text{bpy})$ (bpy = 2,2'-bipyridine) measured across the full chemically relevant range (100–
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22 4000 cm^{-1}), together with their anharmonic DFT assignments. $\text{ReCl}(\text{CO})_3(\text{bpy})$ is a prototypical
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24 member of the rhenium-carbonyl-polypyridine family of versatile redox
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26 photosensitizers/photooxidants and luminescent imaging agents.^{15,16,17} It also is a well-known
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28 photo- and electro-catalyst of CO_2 reduction.^{18,19,20,21} In most cases, TRIR is the technique of
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30 choice to study excited states of $\text{ReCl}(\text{CO})_3(\text{bpy})$ and its congeners, owing to the presence of
31
32 strong $\nu(\text{C}\equiv\text{O})$ IR bands that are highly sensitive to the electron density distribution.^{1,15,22,23,24,25}
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34 In particular, the lowest excited state of $\text{ReCl}(\text{CO})_3(\text{bpy})$ was unambiguously characterized by
35
36 $\nu(\text{CO})$ TRIR spectra as predominantly metal-to-ligand charge transfer (MLCT) and approximately
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38 formulated as $\text{Re}^{\text{II}}\text{Cl}(\text{CO})_3(\text{bpy}^{\bullet-})$.^{14,15,22,23,26} High-frequency IR features of both the electronic
39
40 ground and excited states were assigned by anharmonic DFT calculations, which also identified
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42 bpy-based combination bands occurring unexpectedly close to $\nu(\text{CO})$ features.¹⁴ Far less is
43
44 known about the behavior of bpy-localized and low-frequency skeletal modes whose IR
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46 signatures are much weaker or wholly unavailable. Some of the excited-state bpy-localized
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48 vibrational features were observed in the static transient resonance Raman (TR^2) spectrum of
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3 ReCl(CO)₃(bpy) measured with a 364 nm pump,²⁷ while picosecond temporal evolution of
4 several bpy-localized Raman bands of ReCl(CO)₃(bpy) and [Re(4-Et-pyridine)(CO)₃(bpy)]⁺ was
5 followed by time-resolved resonance Raman spectra (TR³) probed at 400 nm.²⁶ Both
6 experiments took advantage of (pre)resonance enhancement due to a strong $\pi\pi^*(\text{bpy}^{\bullet-})$
7 electronic transition at 373 nm
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15 This study demonstrates the power of combining TR-FSRS experiments in the range of
16 skeletal and ligand-localized vibrations with DFT calculations and 2nd order perturbational
17 anharmonic DFT vibrational analysis in characterizing structural and electronic changes upon
18 excitation and excited-state evolution on the femto-picosecond timescale.
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28 ■ EXPERIMENTAL AND COMPUTATIONAL TECHNIQUES

29 *Materials*

30 ReCl(CO)₃(bpy) was prepared according to a literature procedure²⁸ by a ~3hr reflux of Re(CO)₅Cl
31 and 2,2'-bpy in a 1:1.1 molar ratio (both Sigma-Aldrich) in degassed toluene followed by
32 extensive washing of the precipitated product with toluene and diethylether. Purity was
33 checked by IR and NMR. Nearly saturated solutions in CH₃CN and CD₃CN (Sigma-Aldrich,
34 spectroscopic quality) were used under air atmosphere.
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47 *Femtosecond Stimulated Raman Spectroscopy*

48 The FSRS setup at ELI-Beamlines (Inst. of Physics, Prague) is pumped by a commercial 1
49 kHz titanium sapphire femtosecond amplifier system Femtopower (Spectra-Physics) generating
50 20 fs pulses centered at 800 nm. The beam is split by dielectric beam splitters into three
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3 synchronized beam paths: 1 mJ driving the “actinic pump” generation, 1.5 mJ driving the
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5 “Raman pump” generation, and 200 μJ driving the “probe” generation. Actinic pulses are
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7 converted to 400 nm by second-harmonic generation in a BBO crystal and passed through an
8
9 optical delay line that allows setting their timing relative to probe and Raman pump pulses with
10
11 a sub-10 fs precision. Actinic pulses are attenuated to an average energy of 2 μJ at the sample
12
13 by a gradient neutral-density filter. Raman pump pulses are generated by sending 800 nm, ~ 20
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15 fs driving pulses through a home-built 4f pulse shaper that selects a spectrally narrow interval,
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17 effectively generating pulses approximately 1 nm broad, 2 ps long, and with $\sim 3 \mu\text{J}$ energy,
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19 whose center wavelength is tunable within the $\sim 1000 \text{ cm}^{-1}$ width of the generating 800 nm
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21 pulse. A chopper wheel²⁹ installed in the Fourier plane of the pulse shaper consecutively
22
23 generated 96 different wavelengths of the Raman pump pulse, each shifted by approximately
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25 10 cm^{-1} from the previous one in the 765–835 nm interval. Pulses were adjusted to an average
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27 energy of 3 μJ at the sample by a linear-gradient neutral density filter. The probe is generated
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29 by a two-stage process. A home-built supercontinuum-seeded NOPA converts 800-nm pulses
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31 into 1400-nm pulses that are subsequently focused into a 2-mm sapphire plate, generating the
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33 probe supercontinuum, which is separated from the 1400 nm driving pulses by a dichroic
34
35 beamsplitter. The probe supercontinuum spectrum spans from 350 to 1200 nm and is
36
37 conveniently flat around the 800 nm Raman pump wavelength. The relative polarization of
38
39 Raman pump and probe beams were set parallel by a half-wave-plate in the Raman pump path,
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41 while polarization of the actinic pulse was set to the magic angle (54.7°) relative to the probe
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43 using a half-wave-plate, in order to suppress possible polarization-related effects. The relative
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3 timing of Raman pump and probe pulses is adjusted to provide maximal FSRS signal, which is
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5 known to occur close to, but not exactly at, the perfect temporal overlap.³⁰
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8 After the sample, the probe is split into two copies that are spectrally imaged and
9
10 analyzed by two respective imaging spectrographs (Acton Princeton Instruments) operating in
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12 0-2000 and 2000-4000 cm^{-1} ranges. Each spectrograph is equipped with a FFT CCD 1024 x 58
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14 pixel array camera operating at 1 kHz at full vertical binning, effectively working as a linear
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16 sensor (Entwicklungsbuero Stresing). Both cameras are read simultaneously for each shot,
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18 together with a photodiode signal that records the Raman pump pulse energy. This photodiode
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20 signal is used for synchronization and parallel detection of the 96 individual FSRS experiments
21
22 (each obtained with a differently shifted Raman pump wavelength) in 100 ms cycles, where 96
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24 ms is used for recording FSRS and 4 ms for recording transient absorption. This is a compromise
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26 between the duration of the experiment and the signal intensity since Raman signals are usually
27
28 considerably weaker than transient absorption signals, which therefore require shorter
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30 acquisition time. The 96 individually shifted Raman signals are recombined into a single
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32 spectrum with a highly suppressed baseline and pixelation artifacts by the "watermarking"
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34 approach described elsewhere.²⁹ Each time-delay point is a result of a 1 minute accumulation
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36 time.
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44 For each time delay, a ground- and excited-state Raman, and TA signals are measured.
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46 This is achieved by chopping the actinic pump at 500 Hz. To record both ground- and excited-
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48 state Raman signals for each position of the modulator, the phase of the chopper inserted in
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50 the actinic beam path is flipped by 180° at regular intervals. This "phase flip" approach cancels
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52 out any artifacts related to irregularities in the Raman pulse modulator shape.^{29,31} Each of the
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3 two CCD array cameras records a spectral interval approximately 2000 cm^{-1} wide, covering the
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5 $0\text{--}2000\text{ cm}^{-1}$ and $2000\text{--}4000\text{ cm}^{-1}$ ranges, respectively. The signals are numerically stitched
6
7 together, so the entire $0\text{--}4000\text{ cm}^{-1}$ range is observed simultaneously. Detectors are calibrated
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9 by recording FSRS of a 1:1 (v:v) toluene:acetonitrile mixture with accurately known Raman
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11 spectrum.³²
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15 In present experiments, the probe beam was focused to a spot of $\sim 40\text{ }\mu\text{m}$ diameter at
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17 the sample and overlapped with $\sim 100\text{ }\mu\text{m}$ Raman and actinic pump beams. The delay of the
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19 actinic pump was scanned from 200 ps before to 6 ns after the arrival of the FSRS probe in 134
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21 logarithmically distributed delay times, providing approximately 8 time points for each doubling
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23 of the delay time. Each experiment was repeated several times to verify reproducibility and, for
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25 each data point, a median value was selected for analysis. Sample solutions were flowed in a
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27 $10\times 1\times 1\text{ mm}$ rectangular quartz flow cell (custom-made by Firefly Sci, Inc.). The flow speed was
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29 set to ensure a fresh sample spot for each laser shot with a peristaltic pump (mzr-4622-hs-f
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31 from HNP Mikrosysteme GmbH). Minimal sample damage (below 1%) was verified by
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33 measuring absorption spectra before and after the experiment in a conventional 1 mm quartz
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35 cell (Hellma) in a commercial spectrometer (2800 Shimadzu).
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42 Residual baselines in the data were corrected by fitting 9th order polynomials using the
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44 method of least absolute value residuals. In comparison to the least-square fitting, the baseline
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46 obtained by this method is less sensitive to sharp changes, for example at bases of narrow
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48 peaks. (The least-square procedure by definition fits into the center of the data and thus the
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50 baseline does not follow the pedestals of the peaks but goes through their centers. Corrected
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52 signals then tend to have a Mexican hat shape. This problem does not occur with least absolute
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3 residual fitting where polynomial fitting removes the broadband baseline from narrowband
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5 peaks at their bases.)
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8 Ground-state FSRS spectra labeled "Exp" and "Exp2" are based on the same raw data
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10 but differently analyzed: "Exp" shows data processed by spectral watermarking,²⁹ while "Exp 2"
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12 spectra were obtained by averaging of shifted signals that were numerically aligned according
13
14 to their Raman shift. The latter approach produces a spectrum that is very close to the raw
15
16 single-wavelength FSRS but with an improved fixed-pattern noise as the shifted spectra are
17
18 recorded at varied positions of the detector. In general, watermarking produces a superior
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20 baseline that is, however, prone to specific artifacts when the Raman pulse at 0 cm⁻¹ is
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22 scattered within the watermark. Hence, there are only small differences at higher
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24 wavenumbers, whereas a notable difference occurs below 400 cm⁻¹. In general, this work
25
26 shows that measuring very small Raman shifts with FSRS is possible but extra care is required
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28 when spectral modulation is applied since peak shapes can change as individual shifted FSRS
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30 measurements are in a different state of resonance.³³ It follows that spectral watermarking will
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32 require specific corrections when applied closer to resonance.
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42 *Measuring FSRS at low wavenumbers and over broad spectral ranges*

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45 To measure FSRS over a broad wavenumber range, a 2-stage probe preparation was
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47 used, whereby the probe is generated from a driving beam whose wavelength is beyond the
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49 sensitivity range of the silicon detector. This approach has two key advantages for the FSRS
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51 experiment: It allows generating probe pulses that have a flat spectral profile in the 450–1100
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53 nm interval (or, 350–1100 when CaF₂ is used instead of sapphire) and, at the same time,
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3 exponentially increasing intensity between 1100 and 1200 nm, thus compensating for an
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5 exponential loss of the silicon-detector sensitivity in this range. Note that the spectral intensity
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7 of a single-filament supercontinuum drops very rapidly upon moving from the generating
8
9 wavelength and a relatively flat spectral profile is reached only at a substantial distance. Thus,
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11 FSRS experiments where the Raman pump and the probe-supercontinuum generating pulses
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13 are centered at the same wavelength (often at 800 nm for Titanium Sapphire lasers) operate in
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15 a truncated detection range, as small Raman shifts suffer from an excessive probe intensity,
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17 while highly Raman-shifted peaks suffer from a weak probe intensity. Such experiments have
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19 narrow effective spectral ranges, with only a few Raman signals in the detection optimum. In
20
21 contrast, our experimental setting allows recording vibrations in the 40–4000 cm^{-1} range
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23 simultaneously with excellent homogeneous sensitivity. (Performance in the low-end of this
24
25 range is demonstrated in Figure S9.) This approach is superior to single-stage probe generation
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27 either by a single NOPA³⁴ or by a single supercontinuum process.³⁵ Spectra at low wavenumbers
28
29 can also be recorded by impulsive stimulated Raman experiments performed in the time
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31 domain,^{36,37} however this approach struggles with recording high-energy vibrations since few-
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33 cycle pulses as short as 5 fs are required for exciting vibrations at wavenumbers above 2000
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35 cm^{-1} . Moreover, impulsive Raman spectra have to be corrected for the temporal pulse
36
37 envelope and thus produce patterns that often differ substantially from those recorded by
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39 spontaneous Raman scattering. Furthermore, the time-domain approach needs scanning to
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41 record spectra and is therefore sensitive to laser instability. In contrast, the FSRS approach used
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43 herein allows for simultaneous observation of both low- and high-energy vibrations with a good
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45 agreement with spontaneous Raman spectra for each shot. Typically, few thousands shots are
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3 averaged to achieve a good signal-to-noise ratio, but this process is independent of the short-
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5 term laser instability.
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10 *Computational details*

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13 Calculations were performed using Gaussian 16, Revision A.03 (G16)³⁸ together with the
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15 three-parametrized Becke, Lee, Yang, Park (B3LYP) functional.^{39,40} For the Re atom, we used a
16
17 large basis set (8s7p6d2f1g)/[6s5p3d2f1g] and a standard Stuttgart/Dresden pseudopotential
18
19 for 60 core electrons.^{41,42} For non-metal atoms we used the 6-31+G(d) basis set.⁴³ Solvent
20
21 effects (acetonitrile) were described by the polarizable continuum model (PCM).⁴⁴ The lowest
22
23 triplet excited state was calculated by the unrestricted Kohn-Sham approach (UKS). Calculations
24
25 started from a previously optimized structure¹⁴ that was reoptimized with G16 and PCM-
26
27 CH₃CN. Triplet–triplet electronic excitations were calculated by time–dependent DFT approach
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29 at UKS-optimized geometry.
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35 Anharmonic calculations were based on the second-order vibrational perturbation
36
37 theory (VPT2) model,^{11,13,45,46,47} which provides an accurate description of anharmonic
38
39 vibrational energies and wave functions. Fermi and Darling–Dennison resonances were treated
40
41 by the generalized VPT2 procedure⁴⁸ (GVPT2) on calculated anharmonic potential energy
42
43 surfaces obtained by the deperturbed VPT2 scheme (DVPT2). Cubic and semidiagonal quartic
44
45 force constants were computed by numerical differentiation (with displacements of 0.01 Å) of
46
47 the analytical Hessian along each active normal coordinate. In the first step, a full
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49 dimensionality (FD) calculation included all vibrational modes. Afterwards, large-amplitude
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51 motions (LAMs) were identified and their contributions were skipped from GVPT2 calculations.
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3 Out of the 78 vibrational modes of $\text{ReCl}(\text{CO})_3(\text{bpy})$ 53 and 62 modes were active in calculations
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5 of GS and ES spectra, respectively. The VMS-Draw⁴⁹ graphical user interface was used to
6
7 analyze the outcome of vibrational computations.
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10 11 12 13 ■ RESULTS

14
15 Time-resolved FSRS of $\text{ReCl}(\text{CO})_3(\text{bpy})$ were measured in CH_3CN and CD_3CN solutions
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17 upon 400 nm, 40 fs excitation into the lowest MLCT absorption band. The 800 nm Raman pump
18
19 pulse (2 ps, 16 cm^{-1} fwhm) is out-of-resonance for the ground state whose lowest allowed
20
21 electronic absorption band occurs at 371 nm.^{28,50} On the other hand, the Raman pump falls into
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23 the weak/broad absorption of the lowest ³MLCT excited state that originates from $\pi\pi^*$
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25 transitions localized at the $\text{bpy}^{\bullet-}$ ligand (Figure S1).^{51,52} The broad-band white-light continuum
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27 (Raman probe) was generated using pulses at a wavelength (1400 nm) longer than that of the
28
29 Raman pump in order to achieve a relatively smooth/flat profile in the 800–1200 nm interval
30
31 where the Raman signals occur, thus enabling to measure spectra at small Raman shifts values,
32
33 from ca. 40 cm^{-1} . Additionally, we used watermarking,²⁹ whereby multiple experiments with
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35 slightly shifted Raman wavelengths are performed in parallel and recombined into a single
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37 Raman spectrum with a greatly improved baseline and decreased fixed-pattern noise. These
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39 two technical innovations allowed us to obtain good-quality spectra over a very broad spectral
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41 range.
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52 *Ground- and excited-state Raman spectra and their assignment*
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3 Ground-state FSRS of $\text{ReCl}(\text{CO})_3(\text{bpy})$ spectra are shown in Figures 1 and S2, together
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5 with those calculated using harmonic and anharmonic approximations. The peak wavenumbers
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7 are summarized in Table 1 and selected vibrational modes are visualized in Chart S1.
8
9 Anharmonically calculated wavenumbers and the overall spectral pattern match well the
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11 experimental spectrum, except for the $\nu(\text{CO})$ vibrations whose wavenumbers were calculated
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13 accurately (as compared with IR values¹⁴) but the theoretical Raman intensities are much higher
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15 than the weak signals apparent in CH_3CN (Figure S2). A strong band belonging to bpy-ring CC
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17 and CN stretching vibrations occur at 1600–1605 cm^{-1} whereas the predominantly inter-ring
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19 $\nu(\text{CC})$ band is observed at 1490–1493 cm^{-1} . Inter-ring stretching contributes to several other
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21 modes as well, especially to the intense feature at 1314–1319 cm^{-1} . Re-CO stretching vibrations
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23 are observed at ~ 479 and 500–507 cm^{-1} , usually coupled with ReCO deformations. The Re-Cl
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25 stretch makes the principal contribution to the 239–243 cm^{-1} feature, while also contributing to
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27 the modes at 256–265 and 115 cm^{-1} , where it is usually coupled with deformations of the
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29 Re(bpy) moiety. Few bands deviate from the anharmonically calculated spectrum. Namely, the
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31 calculation overestimates vibrational wavenumbers in the 1550–1650 cm^{-1} range. The feature
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33 observed at 1568 (CH_3CN) and 1557 cm^{-1} (CD_3CN) was thus tentatively attributed to the $\nu(\text{CN},$
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35 CC) mode 64 calculated at 1600 cm^{-1} , with a possible contribution from a 52+20 combination
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37 band calculated at 1581 cm^{-1} . The strong band at 1600–1605 cm^{-1} most likely encompasses
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39 $\nu(\text{CN}, \text{CC})$ modes 66 and 67 calculated at 1622 and 1633 cm^{-1} , respectively. Features at 1368
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41 (possibly solvent) and 915 cm^{-1} also do not match any calculated strong Raman band and their
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43 assignment (Table 1) remains tentative.
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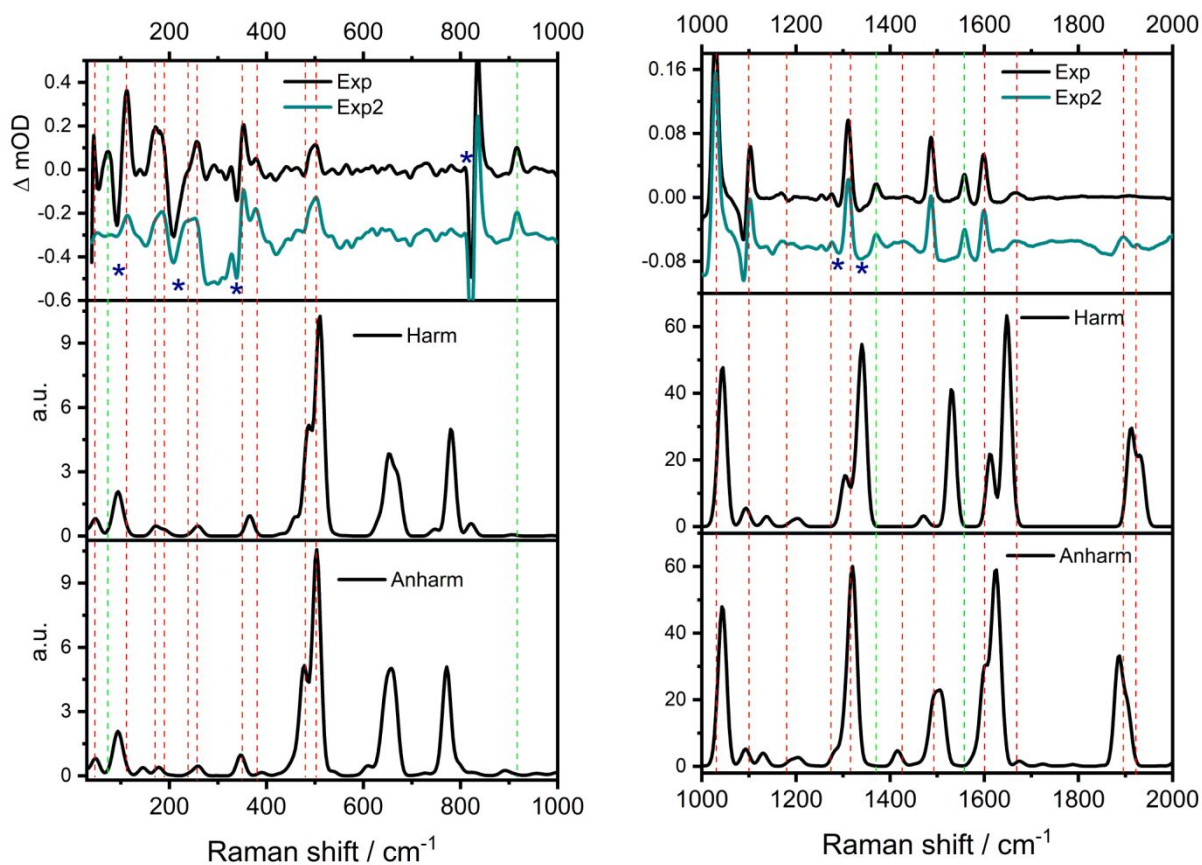


Figure 1. Ground-state FSRS of $\text{ReCl}(\text{CO})_3(\text{bpy})$ in CD_3CN (top), together with harmonically (middle) and anharmonically (bottom) calculated Raman spectra. Exp and Exp2 spectra in the top panel originated from the same raw data that were analyzed using "watermarking" and averaging of shifted signals, respectively. (See the Experimental section.) Red vertical lines connect experimental and corresponding anharmonically (bottom) calculated Raman features. Green vertical lines show experimental Raman bands without obvious calculated counterparts. * denotes residual solvent features and background artifacts. a.u. = arbitrary units. No significant spectral features were observed between 2000 and 4000 cm^{-1} . Spectra measured in CH_3CN are shown in Figure S2.

Table 1. Experimental^a and calculated Raman spectra of ground-state ReCl(CO)₃(bpy).

# ^b	Principal vibrations ^c	Experimental	Harmonic	Anharmonic	Relative int. ^c
70	$\nu(\text{CO})$	2021	2054	2024	20.5
69	$\nu(\text{CO})_{\text{asym,eq}}$	1916	1932	1904	33
68	$\nu(\text{CO})_{\text{ax}} + \nu(\text{CO})_{\text{sym,eq}}$	1894	1911	1884	59.6
	58+17	1666	-	1675	3.2
67	$\nu(\text{CN, CC})$	1605 (1600)	1655	1633	40.8
66	$\nu(\text{CC})_{\text{ring}}$		1647	1622*	78.2
64	$\nu(\text{CN, CC})$	1568 (1557)	1612	1600*	55.9
	52 +20		-	1581	4.4
63	$\nu(\text{CC inter-ring, CC}) + \delta(\text{CH})$	1493 (1490)	1531	1510*	39.7
	58 +12		-	1493	34.4
	40 + 28		(1425)	-	1426
60	$\nu(\text{CN, CC, CC-inter-ring})$	1410 ?	1471	1415*	8.4
59	$\nu(\text{CC}) + \delta(\text{bpy, CH})$	(1368)	1351	1351	1.2
58	$\nu(\text{CC inter-ring, CN}) + \delta(\text{CH})$	1319 (1314)	1340	1319*	100
55	$\nu(\text{CN}), \delta(\text{CH})$	(1275)	1299	1283	8.6
53	$\delta(\text{CH})$	(~1181) ?	1191	1188	3.4
52	$\delta(\text{CH})$	-	1152	1135	1.2
49	$\nu(\text{CC}), \delta(\text{CH})$	(1100)	1093	1093*	10.5
47	$\delta(\text{bpy})_{\text{sym}}\text{-breath} + \delta\text{Rebpy}$	1033 (1030)	1044	1044*	91.9
46	$\delta(\text{bpy})_{\text{antisym}}\text{-breath} + \delta\text{Rebpy}$		1034	1034*	12.4
	28 + 21	(970)	-	975	0.002
41	$\delta(\text{CH})_{\text{sym, out-plane}}$	(915)	909	909	0.1
	20 overtone		-	893	0.3
40	$\delta(\text{CH})_{\text{antisym, out-plane}}$		901	886	0.2
38	$\delta(\text{bpy})_{\text{sym}}\text{-breath}$	767 ?	781	771	10.2
35	$\delta(\text{CH})_{\text{sym}} + \nu(\text{CC inter-ring})$	-	745	727	0.2
32	$\nu(\text{ReN}), \delta(\text{CC})$	-	652	649	6.3
30	$\delta(\text{Re-C-O})$	-	632	607	0.8
28	$\delta(\text{CC, CH})_{\text{antisym, out-plane}}$	-	563	537	0.2
25	$\nu(\text{Re-CO})_{\text{ax}}$ $\delta(\text{Re-C-O})_{\text{eq}}$	507 (500)	510	504*	20.5
23	$\nu(\text{Re-CO})_{\text{eq}}$ $\delta(\text{Re-C-O})_{\text{ax}}$	(479)	486	478*	5.9
	-	432	-	-	
21	$\delta(\text{CC}) + \delta(\text{Rebpy})$	-	460	456	1.4
20	$\delta(\text{CC, CH})_{\text{antisym, out-plane}}$ $\delta(\text{O-C-Re})$	-	456	442	0.4
18	$\delta(\text{CC, CH})_{\text{sym, out-plane}}$	(380)	430	390	0.3
17	$\delta(\text{bpy})_{\text{out-plane}}$	(352)	365	347*	1.9
	-	311 (307)	-	-	

	-	(290)	-	-	
16	$\delta(\text{bpy})_{\text{out-plane}} + \nu(\text{ReCl})$	265 (256)	261	261*	0.4
15	$\delta(\text{bpy})_{\text{out-plane}} + \nu(\text{ReCl})$		259	259*	0.5
14	$\nu(\text{ReCl}) + \delta(\text{Rebpy})$	243 (239)	248	244*	0.3
12	$\delta(\text{bpy})_{\text{sym, out-plane}} + \delta(\text{Rebpy})$	(189) 177 (170)	190	178*	0.8
10	$\delta(\text{bpy})_{\text{antisym, out-plane}} + \delta(\text{ReCl})$	(115)	107	107	0.6
9	$\delta(\text{ReCl}) + \delta(\text{bpy}) + \delta(\text{ReCO})$		100	100	0.5
8	$\delta(\text{bpy}) + \delta(\text{CO})$		95	95	1.1
7	$\delta(\text{CO}) + \delta(\text{ReCl})$		94	94	1.4
6	$\delta(\text{ReCO}) + \delta(\text{CReCl}) + \delta(\text{bpy})$	-	92	92	1
2	$\delta(\text{bpy}) + \delta(\text{ReCO}) + \delta(\text{ReCl})$	(45) ?	48	48	1.7

^a Data from CH₃CN or (CD₃CN) solutions. No significant spectral features were observed between 2000 and 4000 cm⁻¹. ? after an experimental wavenumber indicates a weak or uncertain feature. ^b Normal mode number in the order of increasing frequency. ^c Based on anharmonic calculation. Deformations of the Rebpy moiety ($\delta(\text{Rebpy})$) involve ReN stretches. * Vibration shown in Chart S1.

Excited-state FSRs measured at 60 ps when the ³MLCT state is thermalized^{25,26,53,54} is compared with theoretical spectra in Figures 2, S3. Anharmonic vibrational analysis of the UKS-DFT optimized lowest ³MLCT excited state identified excited-state Raman features and characterized the corresponding vibrations (Table 2, Chart S2). A good match between calculated and experimental frequencies was obtained while the intensity patterns are not directly comparable since experimental intensities are partly affected by resonance with $\pi\pi^*(\text{bpy}^{*-})$ transitions (Figure S1). Thus, the most intense calculated Raman band due to the totally symmetric in-phase $\nu(\text{CO})$ vibration is not observed in the experimental spectrum whereas bpy^{*-} vibrations and some of the low-frequency modes give rise to well-developed signals. Calculations also provided the Duschinsky matrix (Figures 3, S4) that correlates ground- and excited-state vibrations. The matrix shows considerable remixing among CC and CN stretching and CH bending modes of the bpy ligand (55-67) on going to the excited state. For

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3 example, the excited-state mode 67 contains 22 % and 65 % contributions of ground-state $\nu(\text{CC},$
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6 $\text{CN})$ modes 65 and 67, respectively. The predominantly inter-ring CC stretch ground-state mode
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8 58 at 1314–1319 cm^{-1} contributes to excited-state vibrations 57 (26%, at $\sim 1278 \text{ cm}^{-1}$) and 59
9
10 (61%, at 1370 cm^{-1}) and to a host of higher-lying modes. Remixing also occurs between
11
12 $\delta(\text{bpy})/\delta(\text{CH})/\delta(\text{Rebpy})$ modes 40–53, deformation and Re-CO stretching vibrations 20-30, the
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14 group of related $\nu(\text{ReCl})/\delta(\text{Rebpy})$ vibrations 14–16, as well as among low-frequency modes 1–
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16
17
18 10.

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21 Excited-state FSRS shows strong $\nu(\text{CC}, \text{CN})$ and $\nu(\text{CC-ring}, \text{inter-ring})$ features at ~ 1550
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23 and $\sim 1500 \text{ cm}^{-1}$, respectively. The inter-ring CC stretch contributes to vibrations 64, 63, 60, and
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25 59 that occur in the range 1370–1500 cm^{-1} . However, the only modes well visible in the
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27 spectrum are 64 (1502 cm^{-1}) and 60 ($\sim 1420 \text{ cm}^{-1}$). The band due to the principal $\nu(\text{CC inter-}$
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29 $\text{ring})$ mode 59 (1370 cm^{-1}) is barely apparent, in contrast to the corresponding strong GS
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31 feature 58 at 1314–1319 cm^{-1} . On the other hand, the excited-state spectrum shows bands at
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33 ~ 1174 ($\delta(\text{CH})$), 1217 ($\delta(\text{CH})$), and ~ 1278 ($\nu(\text{CC}, \text{CN})$) cm^{-1} that do not have strong counterparts
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35
36 in the ground-state spectrum, whereas the strongest ground-state $\delta(\text{bpy-breathing})/\delta\text{Rebpy}$
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38 feature at 1033 cm^{-1} shifts to $\sim 1008 \text{ cm}^{-1}$ and decreases in intensity. The low-frequency region
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40 exhibits features due to deformation vibrations of the $\text{bpy}^{\bullet-}$ ligand and the $\text{Re}^{\text{II}}(\text{bpy}^{\bullet-})$ chelate
41
42 ring (522-525, 632, ~ 661 , 710 cm^{-1}), an Re-CO stretch at 375, 402-409, 436-443 cm^{-1} , and ReCO
43
44 deformations (436-443, ~ 471 , 539–593 cm^{-1}). The principal mode involving the Re-Cl stretch
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46 was observed at 266–277 cm^{-1} . $\nu(\text{ReCl})$ also contributes to the features at 245–253 and ~ 200
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52 cm^{-1} , coupled with out-of-plane $\text{bpy}^{\bullet-}$ and $\text{Re}^{\text{II}}(\text{bpy}^{\bullet-})$ deformations.
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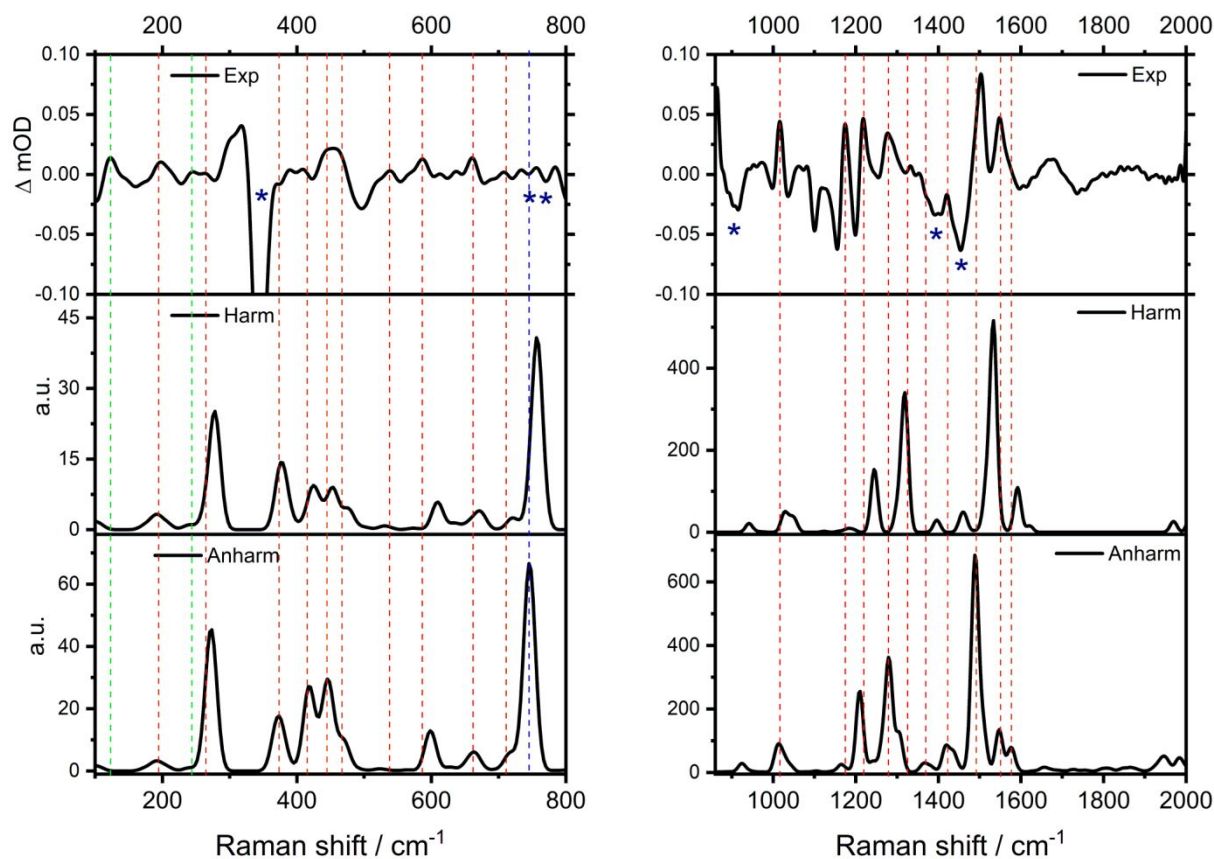


Figure 2. FSRS of the lowest electronic excited state of $\text{ReCl}(\text{CO})_3(\text{bpy})$ in CD_3CN measured 60 ps after 400 nm excitation (top), together with harmonically (middle) and anharmonically (bottom) calculated Raman spectra. Red lines connect experimental and corresponding anharmonically calculated Raman features. Green lines show experimental Raman bands without obvious calculated counterparts. Blue line: Calculated band without an experimental counterpart presumably due to overlapping solvent features and background artifacts. * denotes residual solvent features and background artifacts. No experimental features detected between 2000 and 4000 cm^{-1} . Spectra measured in CH_3CN are shown in Figure S3. (a.u. = arbitrary units)

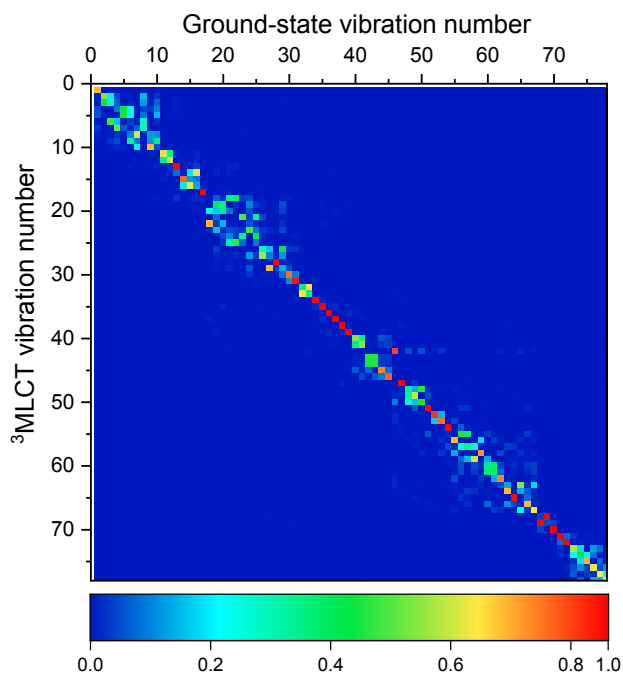
Table 2. Experimental^a and calculated Raman spectra of the lowest electronic excited state $\text{ReCl}(\text{CO})_3(\text{bpy})$.

# ^b	Principal vibrations ^c	Experimental	Harmonic	Anharmonic	Relative int. ^c
70	$\nu(\text{CO})_{\text{sym}}$	2053	2086	2052	100
69	$\nu(\text{CO})_{\text{ax}} + \nu(\text{CO})_{\text{sym,eq}}$	1985	2012	1981	4.7
68	$\nu(\text{CO})_{\text{asym,eq}}$	1940	1969	1945	4.3
	63 + 18	1868 (1884)	-	1865	0.8
67	$\nu(\text{CC}, \text{CN})$	1579 (1577) ^d	1621	1576*	3.6

66	$\nu(\text{CC, CN})$	1548 (1550)	1592	1546*	18.3
64	$\nu(\text{CC inter-ring}) + \nu(\text{CC})$	1500 (1502)	1534	1490*	72.4
63	$\nu(\text{CC, CN, CC inter-ring})$ shoulder	1477 (1482)	1516	1484*	2.1
60	$\delta(\text{CH}) + \nu(\text{CN, CC inter-ring})$	1422 (1421)	1456	1417	11.9
59	$\nu(\text{CC inter-ring}) + \delta(\text{CH})$	(1370)	1396	1363	3.3
57	$\nu(\text{CN, CC})$	1279 (1277)	1318	1280*	52
55	$\delta(\text{CH})$	1217 (1218)	1245	1209*	39
53	$\delta(\text{CH})$	1175 (1173)	1179	1164	3.3
	27 overtone	1057	-	1042	1.9
48	$\nu(\text{CC}) + \nu(\text{CN})$	1008 (1016)	1038	1021*	3.6
47	$\delta(\text{bpy-breath}) + \delta(\text{Rebpy})$		1027	1010*	9.1
	31 + 18	980 (972)	-	977	0.1
	25 overtone	-	-	940	0.3
42	$\delta(\text{bpy-breath})_{\text{antisym}} + \delta(\text{Rebpy})$			923	4
40	$\delta(\text{CH})_{\text{antisym, out-plane}}$	843	836	824	0.3
		815			0.3
38	$\delta(\text{bpy-breath})_{\text{sym}}$	767	757	746	9.3
36	$\delta(\text{bpy})_{\text{out-plane}}$	711 (708)	720	716	0.6
35	$\delta(\text{bpy})_{\text{out-plane}}$	~650, 684 (661)	681	671	0.1
34	$\delta(\text{bpy}) + \delta(\text{Rebpy})$		672	665	0.7
33	$\delta(\text{bpy}) + \delta(\text{Rebpy})$		657	654	0.6
32	$\delta(\text{bpy}) + \delta(\text{Rebpy})$		635	628	0.2
31	$\delta(\text{Re-C-O})$	597 (587)	609	599*	2
30 ^e	$\delta(\text{Re-C-O})$	559 (539)	573?	564?	0.1
28	$\delta(\text{bpy})_{\text{out-plane}}$	525 (522)	529	520	0.1
27	$\delta(\text{Re-C-O}) + \delta(\text{bpy})_{\text{out-plane}}$	-	500	492	0.1
26	$\delta(\text{Re-C-O}) + \delta(\text{bpy})_{\text{out-plane}}$	470 (~472)	477	471*	1.2
25	$\delta(\text{Re-C-O}) + \delta(\text{bpy})$	-	466	463	0.4
24	$\nu(\text{Re-CO})_{\text{eq}} + \delta(\text{Re-C-O})_{\text{ax}} + \delta(\text{Rebpy})$	436 (443)	453	447*	4.1
23	$\delta(\text{bpy})_{\text{out-plane}} + \delta(\text{Re-C-O})$		437	436*	0.7
21	$\nu(\text{Re-CO})_{\text{ax}} + \delta(\text{bpy})_{\text{out-plane}}$	402 (409)	423	418	3.5
18	$\nu(\text{Re-CO})_{\text{eq,antisym}} + \delta(\text{Rebpy})$	(375)	384	379	1
17	$\delta(\text{bpy})_{\text{out-plane}}$		375	370*	2.1
16	$\nu(\text{ReCl}) + \delta(\text{Rebpy})$	277 (266)	278	273*	6.9
15	$\delta(\text{Rebpy}) + \nu(\text{ReCl})$	253 (245)	263	263*	0.4
14	$\delta(\text{bpy})_{\text{out-plane}}$	236	239	239	0.2
13	$\delta(\text{bpy})_{\text{out-plane}}$	213	206	206	0.2
12	$\delta(\text{bpy})_{\text{out-plane}} + \delta(\text{Re-Cl})$	200 (198)	191	191*	0.4
11	$\delta(\text{bpy})_{\text{out-plane}} + \delta(\text{Rebpy})$		175	175	0.1
10	Deformation	128 (122)	106	106	0.1

^a Data from CH₃CN or (CD₃CN) solutions. No features detected between 2000 and 4000 cm⁻¹. ^b Normal mode number in the order of increasing frequency. ^c Based on anharmonic calculation.

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3 Deformations of the Rebpy moiety ($\delta(\text{Rebpy})$) involve ReN stretches. ^d Determined by Gaussian
4 decomposition, see the text. ^e Tentative assignment (calculated with a very small intensity). *
5 Vibration shown in Chart S2.
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31 **Figure 3.** Duschinsky matrix of anharmonically calculated vibrations of $\text{ReCl}(\text{CO})_3(\text{bpy})$ in the
32 ground- and lowest ³MLCT states. The matrix shows excited-state vibrations as a linear
33 combination of ground-state vibrations (horizontally) and vice-versa (vertically). The
34 corresponding shift-vector diagram is shown in Figure S5.
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38 Time-resolved excited-state Raman spectra (Figures 4, S6) show dramatic changes in the
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40 1450–1600 cm^{-1} region where a group of features due to high-frequency $\text{bpy}^{\bullet-}$ CC and CN
41 stretching vibrations 63–67 emerges between 150 and 200 fs and then grows over the next few
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43 tens of picoseconds (Figures 5A, B). The integrated area of the corresponding bands grows with
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45 a biexponential kinetics (380 fs, 65%; 21 ps, 35%; Figures 5C and S7). Bandwidths show a small
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47 initial rise followed by narrowing with a maximum at ~ 3 ps (for the 1551 cm^{-1} band, Figure 5D).
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49 The peak maximum of the strongest band shifts from 1496 cm^{-1} at 200 fs to 1502 cm^{-1} at 30 ps
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51 and later. The ~ 1546 cm^{-1} feature undergoes a small upshift and band-shape changes. More
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pronounced restructuring of the 1450–1600 cm^{-1} spectral pattern takes place at the earliest investigated times, from 40 to 200 fs (Figure 5B). The initial spectrum recorded at 40 fs shows spectral features at ca. 1486, 1514, 1532, and 1552 cm^{-1} that all gradually shift to higher wavenumbers. The 1514 cm^{-1} band concomitantly decreases in intensity and eventually (200–300 fs) disappears, whereas the latter two merge into the 1546 cm^{-1} feature showing a ~ 1573 cm^{-1} shoulder. Mid-range spectral features are largely developed already at 150 fs and show only limited dynamics, usually small picosecond upshifts and growth, commensurate with the ~ 21 ps growth component identified in the 1450–1600 cm^{-1} range. This is the case, for example, of the bands at 1212 and 1273 cm^{-1} that shift to ~ 1217 and ~ 1278 cm^{-1} , respectively, while that at 1171 cm^{-1} moves less, to 1174 cm^{-1} . More interesting dynamics occurs in the low-frequency range (Figure 6), where the features at 583 and 665 cm^{-1} (in CD_3CN) and 560–585 cm^{-1} (CH_3CN) decrease in intensity during the first 300 fs whereas the lowest band increases and shifts from ~ 112 (at 150 fs) to 124 cm^{-1} during the first 2 ps. Early band restructuring around 200 and ~ 580 cm^{-1} will be discussed below, in the context of intersystem crossing.

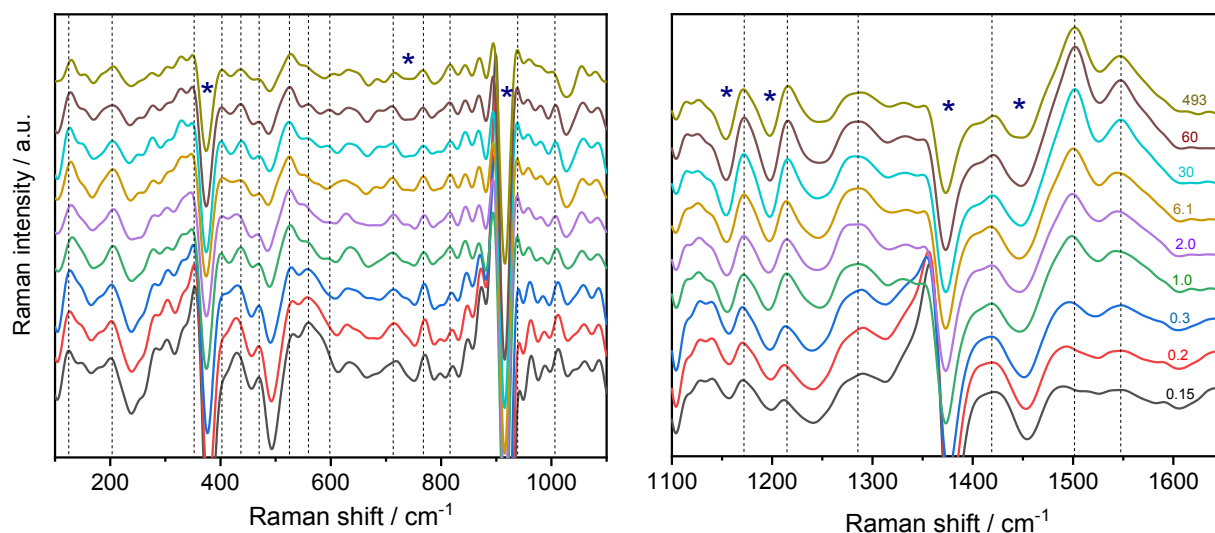


Figure 4. Time evolution of FSRS of $\text{ReCl}(\text{CO})_3(\text{bpy})$ in CH_3CN measured (from bottom to the top) at 0.15, 0.2, 0.3, 1.0, 2.0, 6.1, 30, 60, and 493 ps. The spectra are offset by a constant amount for better visibility. The dotted lines show band positions in the 60 ps spectrum. * Solvent or background features. Spectra in CD_3CN are shown in Figure S6.

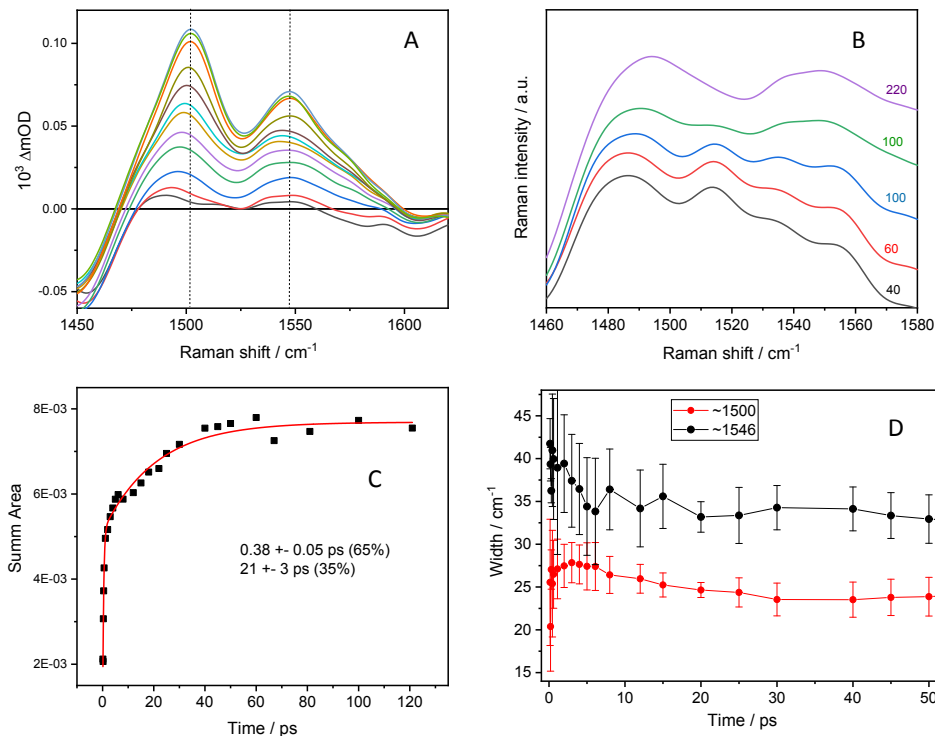


Figure 5. Dynamics of Raman bands in the 1450–1600 cm^{-1} range measured in CH_3CN . A: Time-resolved spectra adjusted to a common zero-signal level. Time delays from bottom up: 0.15, 0.20, 0.30, 0.45, 0.61, 1.1, 2.0, 6.1, 14.9, 30, 60, 122 ps. The dotted lines show band positions in the 60 ps spectrum. B: Detail of the spectral evolution from 40 to 220 fs; spectra are offset by a constant amount. C: Time-dependence of the sum of band areas in the 1450–1600 cm^{-1} range. (Time-dependence of the $\sim 1500 \text{ cm}^{-1}$ band area alone is shown in Figure S7.) D: Time-dependence of the widths (fwhm) of ~ 1500 and 1546 cm^{-1} Raman features. (Band areas and widths were obtained by Gaussian decomposition.)

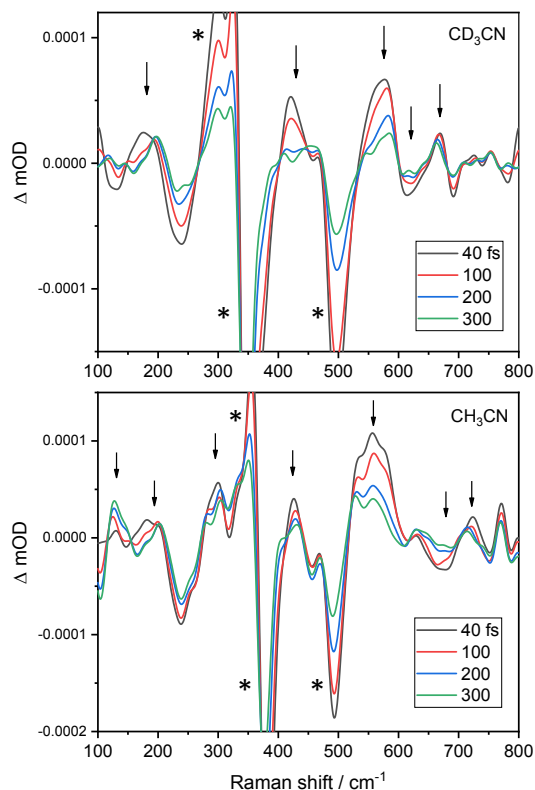


Figure 6. Early FSRS evolution of $\text{ReCl}(\text{CO})_3(\text{bpy})$ in CD_3CN (top) and CH_3CN (bottom). Spectra are adjusted to a common zero-signal level. * denote incompletely subtracted / shifted solvent bands. The spectra were not corrected for the difference in Raman pump absorption between actinic-pumped and non-actinic pumped FSRS that causes intensity variations of the negative solvent peaks whereas positive excited-state feature are affected much less since the ground-state $\text{ReCl}(\text{CO})_3(\text{bpy})$ is several orders of magnitude weaker.

■ DISCUSSION

Ground- and excited-state Raman spectra (FSRS) measured over a full relevant spectral range together with a computational anharmonic vibrational analysis characterize bonding and structural changes upon excitation, while the temporal evolution of the spectra provides information on excited-state relaxation processes that take place on femtosecond to early picosecond timescale.

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3 Calculations show that most vibrational modes are delocalized over several bonds and
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5 molecular fragments (Charts S1, S2). Nevertheless, it is possible to identify groups of vibrations
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7 of similar principal contributions (Tables 1, 2). Going up from the lowest energies, these are bpy
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9 and ReCO deformations coupled with Re-Cl stretches, deformations coupled with Re-CO
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11 stretches, a group of bpy and Re(bpy) deformations (the latter involving Re-N stretching
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13 motions), C-H deformations, inter-ring CC stretch coupled with CC and/or CN stretches of the
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15 bpy ligand, and CC/CN stretching motions of the aromatic rings. CO vibrations around 2000 cm^{-1}
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17 ¹ give rise only to very weak features in the ground-state spectrum. They are entirely absent in
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19 the excited-state spectra, presumably due to the lack of resonance enhancement. FSRS peak
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21 wavenumbers in the high-frequency range agree with those observed in TR³ spectra of
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23 ReCl(CO)₃(bpy).²⁶ The relative band intensities are, however, different because the TR³ spectra
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25 were measured using 400 nm Raman pump whose proximity to the most intense excited-state
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27 electronic absorption band at 373 nm causes much stronger resonance enhancement than 800
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29 nm pumping, where the transient absorption is much weaker (Figure S1C, oscillator strengths in
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31 the legend).^{26,51,52} Interestingly, excited-state FSRS frequencies and intensity patterns of
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33 ReCl(CO)₃(bpy) at 60 ps are very similar to those measured at 100 fs and later for [Ru(bpy)₃]²⁺ in
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35 the 1100–1700 cm^{-1} range using a virtually identical pump wavelength (801 nm).⁵⁵ The close
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37 similarity of excited-state bpy-based Raman features of the complexes with one (Re) and three
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39 bpy ligands (Ru) shows that the charge localization at a single bpy in ³MLCT-excited [Ru(bpy)₃]²⁺
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41 occurs in much less than 100 fs.

52 Shifts of Raman features from the ground-state spectrum to the 60 ps spectrum of the
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54 relaxed lowest excited state are in agreement with bonding changes expected for the
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3 ReCl(CO)₃→bpy CT character of the lowest excited state:^{15,56,57,58,59,60} The bpy-localized LUMO
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5 that becomes singly populated in the excited state is π -bonding with respect to the inter-ring C-
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7 C bond and π -antibonding toward the ring CN and CC bonds (Figure S8).⁵⁷ Accordingly, the
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9 predominantly inter-ring ν (CC) ground-state mode 58 shifts ~ 52 cm⁻¹ higher upon excitation
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11 (contributing 61% to the excited-state mode 59, based on the Duschinsky matrix). Modes 60
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13 and 63, which also have a ν (CC-inter-ring) contribution, transform to 60+61 and 64,
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15 respectively, in the excited state. Each occur ca. 10 cm⁻¹ higher than in the ground state. Bands
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17 due to predominantly intra-ring CC and CN stretching vibrations shift downwards upon
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19 excitation because of a LUMO π^* character. This is the case of the ground-state mode 66 that
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21 amounts to 69% of the excited state mode 66, which lies ca. 55 cm⁻¹ lower. Frequencies of the
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23 modes with significant ν (Re-CO) contributions, namely 23 and 25 (that remix to form excited-
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25 state modes 21 and 24) decrease on average by ~ 68 cm⁻¹. The ν (Re-C) downshift is
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27 complementary to the upshift of ν (C \equiv O) vibrations that has been amply demonstrated by TRIR
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29 spectroscopy.^{15,22,23,26} Both these effects are caused by decreased Re→CO π back-bonding in
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31 the ³MLCT excited state due to depopulation of the Re-CO π -bonding / C \equiv O π -antibonding
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33 HOMO (Figure S8), weakening and strengthening Re-CO and C \equiv O bonds, respectively.
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35 Downshifting ν (Re-CO) Raman features upon excitation provides additional evidence for the
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37 principal Re(CO)₃→bpy contribution to the lowest excited state. It also agrees with the
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39 calculated lengthening of axial and equatorial Re-CO bonds when going to the lowest excited
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41 state by 0.048 and 0.041 Å, respectively.⁶¹ On the other hand, modes involving the Re-Cl
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43 stretching motion shift up by ca. 10 cm⁻¹, which is attributable to the depopulation of the Re-Cl
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45 π -antibonding Re(d π)-Cl(p π) HOMO (Figure S8). In particular, the ν (ReCl)-containing ground-
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3 state modes 14-16 participate in excited-state $\nu(\text{ReCl})$ modes 15 and 16 that lie, on average lie
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5 10 cm^{-1} higher. The upshift of $\nu(\text{ReCl})$ vibrations upon excitation is the third experimental piece
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7 of evidence for the $\text{Cl} \rightarrow \text{bpy}$ CT contribution to the excited-state wave function, after the TRIR
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9 spectra of $\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})$ and time-resolved X-ray absorption of $\text{ReBr}(\text{CO})_3(\text{bpy})$.^{57,58,59}
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13 The temporal evolution of the Raman spectra (Figures 4-6, S6) provides insight into the
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15 mechanism of the lowest excited-state population and its relaxation. Interestingly, individual
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17 Raman bands show different dynamics. High-frequency bands due to bpy-localized CC, CN, and
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19 inter-ring C-C stretching vibrations in the $1450\text{--}1600 \text{ cm}^{-1}$ range are initially nearly absent
20
21 (Figure 5). At 40-100 fs, four very weak bands are observed that blue-shift and merge into two
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23 broad features between 200 and 300 fs (Figure 5B). Subsequently, they grow with
24
25 biexponential kinetics (0.38 and 21 ps), eventually becoming the strongest features in the 60-ps
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27 spectrum of the relaxed $^3\text{MLCT}$ state. This behavior cannot be attributed to increasing
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29 resonance enhancement as the transient absorption at and around the 800 nm Raman pump is
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31 weak and partly decays during the first 2.5 ps (Figure S1). Femtosecond band restructuring was
32
33 also observed for some of the low-frequency Raman bands, namely in the region of
34
35 $\nu(\text{ReCl})/\text{deformation}$ vibrations around $190\text{--}200 \text{ cm}^{-1}$, and $\delta(\text{Re-C-O})$ bending vibrations around
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37 $420\text{--}440$ and $520\text{--}600 \text{ cm}^{-1}$ (Figure 6). This mode-specific dynamics suggests that the electronic
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39 wave function (i.e., the excited-state character) changes in the course of relaxation. Initial time
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41 evolution in the $1450\text{--}1600 \text{ cm}^{-1}$ spectral range agrees with the ultrafast fluorescence decay
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43 kinetics^{52,61} whose 85 and 340 fs lifetimes were attributed to the intersystem crossing (ISC)
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45 from the optically populated $^1\text{MLCT}$ to an intermediate $\pi\pi^*\text{-bpy}$ intraligand (^3IL) and to the
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47 lowest $^3\text{MLCT}$ excited states, combined with a $^3\text{IL} \rightarrow ^3\text{MLCT}$ conversion. This three-state ($^1\text{MLCT}$,
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3 $^3\text{MLCT}$, ^3IL) model is a simplification since intersystem crossing actually proceeds through a
4 manifold of intermediate states that arise from spin-orbit splitting of a number of intermediate
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6 $^3\text{MLCT}/^3\text{IL}$ states.^{50,62,63,64,65,66,67} Quantum mechanical simulations of ultrafast excited-state
7
8 dynamics of $\text{Re}(\text{halide})(\text{CO})_3(\text{bpy})$ complexes indicate that the initial ISC steps from the optically
9
10 populated $^1\text{MLCT}$ occur in less than 20 fs. A more detailed ISC mechanistic picture was obtained
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12 by full-dimensional excited-state dynamics simulations of an analogous
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14 $[\text{Re}(\text{imidazole})(\text{CO})_3(1,10\text{-phenanthroline})]^+$ complex, suggesting a two-phase ISC to the lowest
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16 triplet state.⁶³ In particular, a dynamic equilibrium between triplet and singlet MLCT states is
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18 established in less than 10 fs ("prompt ISC"). Then, convoluted intramolecular vibrational
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20 energy redistribution (IVR) and internal conversion shifts this equilibrium toward the lowest
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22 $^3\text{MLCT}$ state with a hundreds-of-femtoseconds time constant ("retarded ISC"). The latter
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24 process involves a gradually changing excited-state wave function whereby the IL ($\pi\pi^*$ -bpy)
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26 contribution decreases and the MLCT character increases.⁶³ Our FSR dynamics lends support
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28 to this model: The "instantaneous" change of the excited-state wave function is responsible for
29
30 the presence of most of the excited-state Raman features in a few tens of femtoseconds,
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32 whereas the 40–200 fs restructuring of the $\nu(\text{CC,CN}) / \nu(\text{C-C})_{\text{inter-ring}}$ group of bands and its
33
34 subsequent ~ 400 fs growth/upshift are attributable to the "retarded" ISC component. The
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36 $\nu(\text{CC,CN})/\nu(\text{C-C})_{\text{inter-ring}}$ Raman features in the 1450–1600 cm^{-1} range are characteristic of the
37
38 bpy $^{\bullet-}$ ligand and therefore develop and grow in intensity as the excited-state wave function
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40 acquires more $\text{ReCl}(\text{CO})_3 \rightarrow \text{bpy}$ CT character. This process continues well into the picosecond
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42 time domain (21 ps rise) as the solvational and vibrational relaxation drives the intramolecular
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44 charge separation further. These Raman dynamics are consistent with the picosecond growth of
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3 a bpy^{*}-specific ~380 nm band in the TA spectra^{26,52} and with the behavior of $\nu(\text{C}\equiv\text{O})$ features in
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5 TRIR spectra that shift to higher wavenumbers with 1.5 and 12.6 ps time constants and also
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7 indicate the presence of another excited state with more ³IL character.^{26,52,68} FSRS dynamics in
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9 the low-frequency range mostly concerns features due to vibrational modes that involve $\nu(\text{Re-}$
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11 $\text{Cl})$ and $\delta(\text{Re-C-O})$ motions that were found⁶⁹ to be strongly coupled to the ISC process. In fact,
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13 the 40–100 fs spectra show shallow shifting minima at 130–160 and ~690 cm^{-1} that develop
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15 into weak positive features in few hundreds of femtoseconds. These minima might arise from
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17 inverse Raman scattering³⁴ due to vibrations that were activated³⁴ in the course of ISC, as has
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19 been predicted theoretically.⁶⁹ Other spectral features exhibit very limited dynamics, usually
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21 small picosecond upshifts and growths, generally commensurate with the ~21 ps growth
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23 component identified in the 1450–1600 cm^{-1} range and mostly attributed to solvational
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25 relaxation. Interestingly, the FSRS excited-state dynamics of $\text{ReCl}(\text{CO})_3(\text{bpy})$ is more complex
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27 than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ that shows⁵⁵ a monotonous ~110 fs growth of bpy^{*} features. The
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29 difference is attributable to the time-dependent mixing of IL($\pi\pi^*$ -bpy) and CT characters in the
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31 lowest excited state of the rhenium complex, in contrast to a virtually pure MLCT character in
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33 the ruthenium case. Furthermore, the low-symmetry and the presence of ligands with different
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35 polarities and solvation properties make $\text{ReCl}(\text{CO})_3(\text{bpy})$ much more susceptible to solvation
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37 dynamics.
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50 ■ CONCLUSIONS

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3 Time-resolved FSRS of the lowest excited state of a prototypical organometallic
4 photosensitizer/photocatalyst $\text{ReCl}(\text{CO})_3(\text{bpy})$ measured from ~ 40 to 2000 cm^{-1} with ca. 40 fs
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8 time resolution have demonstrated that:

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10 - Good quality FSRS can be measured in the low-wavenumber region ($40\text{--}800 \text{ cm}^{-1}$) when the
11 Raman probe continuum is generated with laser pulses of a wavelength (1400 nm) substantially
12 longer than that of the Raman pump (800 nm). "Watermarking",²⁹ whereby a set of spectra
13 measured at 96 slightly different Raman pump wavelengths is used to reconstruct the final
14 spectrum, improves the experiment sensitivity, background rejection, and the S/N ratio.
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22 - Anharmonic calculations based on DFT and second-order vibrational perturbation theory
23 provide vibrational frequencies that match the experimental Raman shift wavenumbers with
24 accuracy sufficient to interpret experimental spectra, identify weak features, and with the
25 possibility to predict spectra of electronically excited species and photochemical intermediates.
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30 - Shifts of Raman features upon excitation ($\nu(\text{ReCl})$ and $\nu(\text{CC-inter-ring})$ upwards, $\nu(\text{CC, CN})$ and
31 $\nu(\text{Re-C})$ downwards) agree with the predominant $\text{ReCl}(\text{CO})_3 \rightarrow \text{bpy}$ CT character of the lowest
32 excited state, demonstrating the diagnostic value of low-frequency Raman modes in excited-
33 state characterization and the need for reliable assignment provided by anharmonic
34 calculations.
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40 - Temporal evolution of FSRS features is mode-specific and provides information on the
41 dynamics and mechanism of the population of the lowest excited state and its relaxation,
42 namely the development of the charge separation in the relaxed MLCT state.
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3 FSRS experiments coupled with perturbational anharmonic calculations emerge as a promising
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5 tool to investigate the rich excited-state chemistry of Re carbonyl-diimine photosensitizers and
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7 photocatalysts.
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30 Notes

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41 ■ ASSOCIATED CONTENT

42 Supporting Information Available

43 Transient absorption spectra, ground- and excited-state FSRS in CH₃CN, detailed Duschinsky
44 matrices, time-resolved FSRS in CD₃CN, visualization of selected ground- and excited-state
45 vibrations.
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47 This information is available free of charge via the Internet at <https://pubs.acs.org/>.
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