Supplementary Information for

Vibrational Coherence in the Excited State Dynamics of $Cr(acac)_3$: Identifying the Reaction Coordinate for Ultrafast Intersystem Crossing

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Experimental Procedures.

Ultrafast Absorption Spectroscopy. Femtosecond pump-probe transients employing ~ 50 fs optical pulses were recorded using the dynamic-absorption technique, in which the probe beam is dispersed in a grating monochromator after passing through the sample.[1-3] In this work, the pump and probe pulses were obtained from the signal-beam output of an optical parametric amplifier (Coherent OPA 9450), which was pumped by an amplified Ti:sapphire laser (Coherent Mira-seed oscillator and a modified Coherent RegA 9050 regenerative amplifier, with Coherent Verdi V5 and V10 pump lasers, respectively). The laser was operated at a repetition rate of 250 kHz. The pump and probe pulses were corrected for group-delay dispersion on the way to the sample by a SF10 Brewster prism-pair pulse compressor. The pump-probe time delay was scanned using a rapid-scanning delay stage (Clark-MXR, ODL-150) in a modified Mach-Zehnder interferometer with confocal sample and autocorrelation-crystal positions. Calcite polarizers and wave plates in the pump and probe beams set their planes of polarization at 90˚; after passing through the sample, the probe beam was analyzed by another calcite polarizer oriented 90˚

relative to the pump-beam's plane of polarization, and then it was passed through a monochromator (Spex 270M, 4-nm bandpass) and detected by an amplified photodiode (Thorlabs PDA55). The slits of the monochromater were adjusted to obtain a fairly narrow bandpass (4 nm) compared to the width of the laser's spectrum. This approach is similar to that used by Champion and co-workers in their studies of low-frequency vibrational coherence in heme proteins.[4-6] The pump-probe signal was obtained from the photodiode signal using a lock-in amplifier (Femto LIA-MV-200-H); the pump beam was modulated at 50 kHz by a photoelastic modulator (Hinds Instrumentation).

Ultrafast transient absorption data with ~ 100 fs pulse duration were collected as follows. A Ti:sapphire oscillator (Coherent Mira) is pumped at 5.4 W (Coherent Verdi), producing modelocked pulses centered at 803 nm with a FWHM of 13.5 nm at an repetition rate of about 76 MHz. These pulses are fed into a cavity containing a stretcher/compressor and regenerative amplifier (Positive Light Spitfire), pumped by a Coherent Evolution. The output of the regenerative amplifier is again 800 nm, ~100 fs pulses at kilohertz repetition rate. Approximately 70% is fed into an OPA (TOPAS) for generating the appropriate pump wavelength, while the remaining 30% is used to generate the white light continuum (CaF_2 or sapphire) used for the probe pulse. The pump traverses a delay line (Aerotech ATS100-200 with a Unidex 100 motion controller), providing the timing for the experiment. The full white light continuum can be used as a probe for full spectral transient studies, or a 10 nm bandpass filter can be employed to select a probe wavelength for a “single-wavelength” kinetic trace. In the visible, pump powers of 6-7 μJ/pulse are used, while exciting in the ultraviolet requires smaller energies, approximately 1-3 μJ/pulse. Samples were prepared in 1 mm pathlength cells so that the absorbance is 0.4 - 0.7 at the excitation wavelength. A lock-in amplifier and chopper are employed to achieve reasonable S/N, and detection is carried out with two avalanche photodiodes.

Transient full spectra were collected using a fiber-optic cable connected to a Hamamatsu HC233-0900 spectrograph. The spectrograph employs a diode array (C5964 NMOS), upon which the collected photons are imaged after dispersion via a grating. The data was collected in the absence of lock-in detection. Scans of background pump scatter, called dark scans, are collected before the experiment is carried out. Background scans, corresponding to negative times, are collected at the beginning of each scan, and the dark and background scans are both subtracted to calculate the final transient spectra.

Data Analysis. The kinetic trace of Figure 3 was obtained by subtracting an exponential decrease in excited state absorption with a time constant of 320 fs to obtain a flat baseline. This time constant is on the appropriate time scale for intramolecular vibrational redistribution processes. Fitting of the oscillatory component (the residual after subtraction of the exponential components) was accomplished with a program of local origin, and has been described in detail elsewhere.[7] Briefly, the oscillatory residuals were fit with a multicomponent model the contains both slowly damped and rapidly damped components. The slowly damped components were modeled as a simple damped cosinusoid, while the rapidly damped components were modeled in the time domain with inhomogeneously broadened components with asymmetric Gaussian lineshapes. The redder probe (Figure S2) reveals similar oscillatory kinetics as Figure 2, and a 1.6 ps excited-state absorption decay was subtracted from these data. The data acquired with the integrated probe pulse (Figure S3) was fit with a biexponential function with time constants of τ_1= 50 fs and τ_2= 1.3 ps.

For data collected with ~ 100 fs resolution labview programs of local origin were used to process all of the data. In general, fitting of single wavelength kinetic traces with $\tau >$ 500 fs was carried out with an exponential function with an additional y-offset. Fitting was started at 300 fs, past the solvent cross-correlation signal. Sub-ps full spectra must be corrected for the chirp associated with the probe pulse.

References

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Figures.

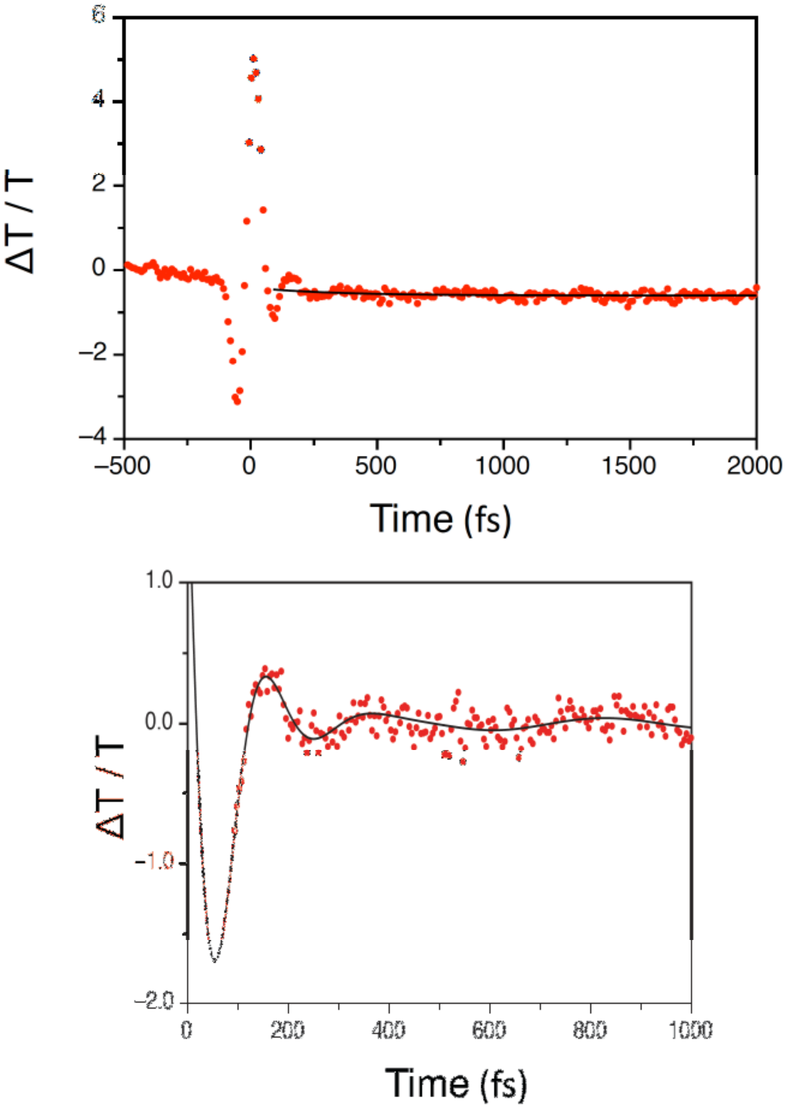

Figure S1. Kinetic trace for Cr(acac)$_3$ pumped at 600 nm and probed at 592 nm. A monoexponential rise in excited state absorption (τ = 320 fs) was subtracted from the raw data (top) to obtain a flat baseline. The residual (bottom) was then fit with two damped oscillatory components having ω_1 = 164 cm^{-1} (τ_{damp} = 70 fs) and ω_2 = 75 cm^{-1}; ω_2 contributes less than 2% to the fit (i.e., $A_{\omega1}/ A_{\omega2} \approx 60$).

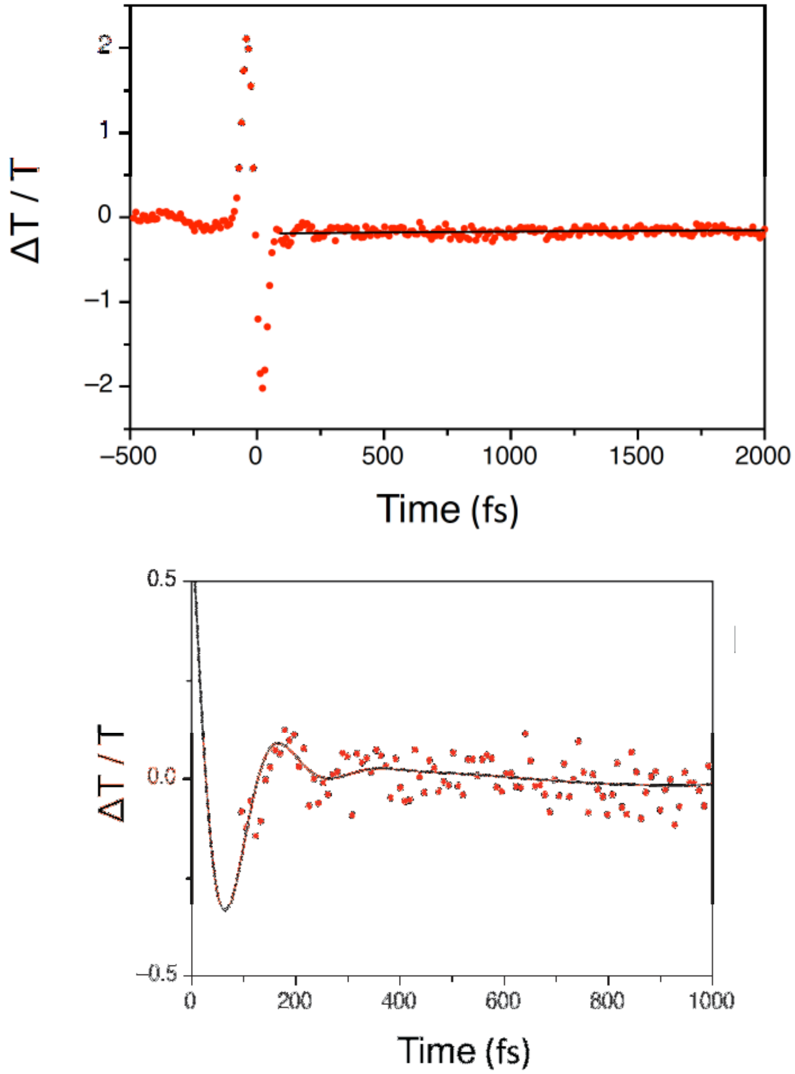

Figure S2. Kinetic trace for Cr(acac)$_3$ pumped at 600 nm and probed at 608 nm. A monoexponential rise in excited state absorption ($\tau = 1.6$ ps) was subtracted from the raw data (top) to obtain a flat baseline. The residual (bottom) was then fit with two damped oscillatory components with $\omega_1 = 165$ cm^{-1} ($\tau_{damp} = 70$ fs) and $\omega_2 = 28$ cm^{-1}; ω_2 contributes less than 3% to the fit (i.e., $A_{\omega 1}/ A_{\omega 2} \approx 34$).

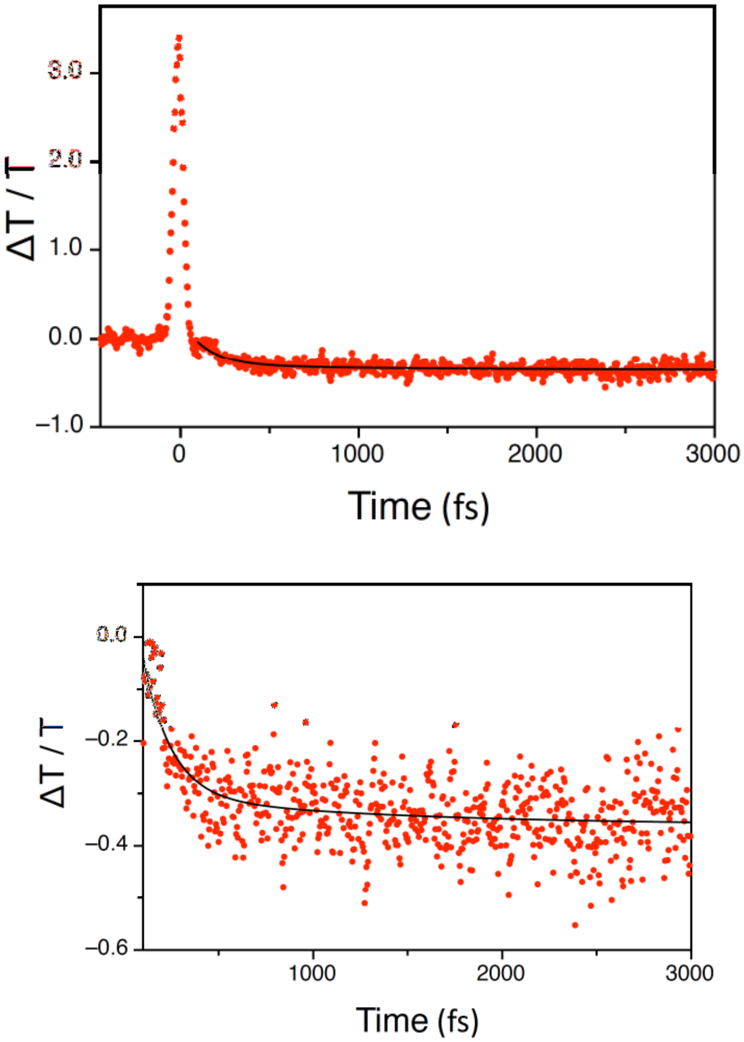

Figure S3. Kinetic trace for Cr(acac)$_3$ pumped at 600 nm and utilizing the integrated probe pulse centered at 600 nm (top). The data were fit with a biexponential kinetic model with τ_1 = 50 fs and τ_2 = 1.3 ps, corresponding to a rise in excited-state absorption (bottom). The second component is consistent with the previously reported time constant for vibrational relaxation in the ^{2}E state; the origin of the process associated with τ_1 will be the subject of a future report.

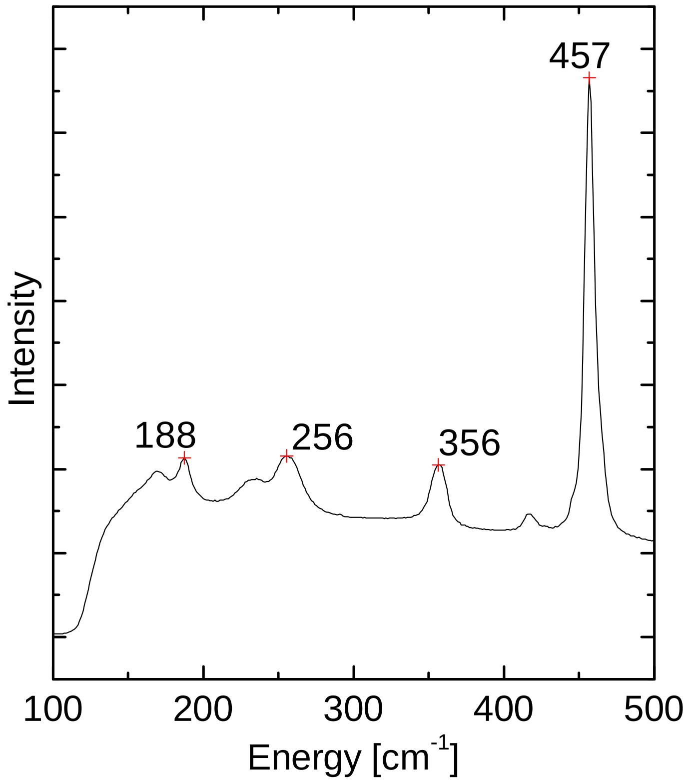

Figure S4. Low-frequency portion of the Raman spectrum of Cr(acac)$_3$, revealing ground state frequencies that correspond to the calculated M-L active modes of Figure 4.

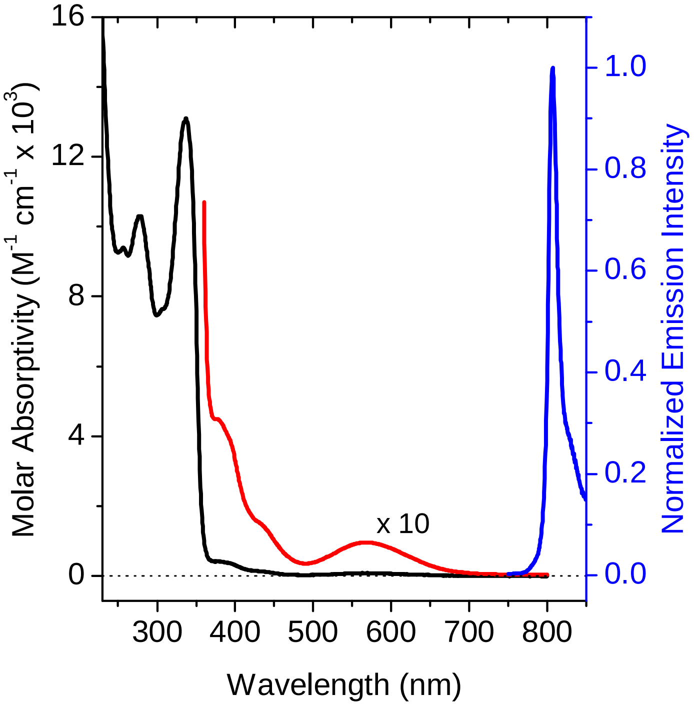

Figure S5: Absorption and emission spectra of Cr(t-Bu-acac)$_3$ acquired in dichloromethane and an 80 K optical glass of 2-methyltetrahydrofuran, respectively.