Vibrational coherence in the excited state dynamics of Cr(acac)$_3$: probing the reaction coordinate for ultrafast intersystem crossing†

Joel N. Schrauben, Kevin L. Dillman, Warren F. Beck and James K. McCusker*

Received 12th April 2010, Accepted 29th May 2010
DOI: 10.1039/c0sc00262c

Vibrational coherence was observed following excitation into the lowest-energy spin-allowed $^4A_2 \rightarrow ^4T_2$ ligand-field absorption of Cr(acac)$_3$. The transient kinetics were fit to a rapidly damped 164 cm$^{-1}$ oscillatory component, the frequency of which is not associated with the ground state of the molecule. The signal is assigned as an excited-state vibrational coherence; the timescale of the event suggests that this vibrational coherence is retained during the $^4T_2 \rightarrow ^2E$ intersystem crossing that immediately follows $^4A_2 \rightarrow ^4T_2$ excitation. DFT calculations indicate that the 164 cm$^{-1}$ oscillation likely corresponds to a combination of Cr–O bond stretching in the ligand-field excited state as well as large amplitude motion of the ligand backbone. This hypothesis is supported by ultrafast time-resolved absorption measurements on Cr(t-Bu-acac)$_3$ (where t-Bu-acac is the monoanionic form of 2,2,6,6-tetramethyl-3,5-heptanedione) – an electronically similar but more sterically encumbered molecule – which exhibits a $^4T_2 \rightarrow ^2E$ conversion that is more than an order of magnitude slower than that observed for Cr(acac)$_3$. These results provide important insights into the nature of the reaction coordinate that underlies ultrafast excited-state evolution in this prototypical coordination complex.

Introduction

The development of ultrashort laser pulses has revolutionized the study of chemical dynamics by allowing detection of the formation and decay of transient species in chemical reactions that are triggered by the absorption of light. One of the more widely examined phenomena deals with the creation of vibrational coherence, in which a system is excited with sufficient bandwidth to yield an in-phase superposition of multiple vibronic states (a so-called wavepacket). Even in large molecules, the vibrational modes associated with the reaction coordinate of photochemical transformations can be detected in terms of vibrational coherence either on the potential energy surface of the Franck–Condon state or on that of the product state. In this report, we document an unusual observation of vibrational coherence in the excited ligand-field state manifold of a simple coordination complex. The data indicate that vibrational coherence is created upon impulsive excitation and is retained during the course of an ultrafast intersystem crossing (ISC) event. More significantly, an analysis of these observations coupled with results on a related compound have provided unique insights into the nature of the vibrational mode(s) coupled to the excited-state dynamics, in effect allowing us to identify the reaction coordinate associated with this sub-picosecond photophysical transformation.

Experimental section

Sample preparation

General. Cr(acac)$_3$ was purchased from Aldrich and recrystallized twice from benzene/petroleum ether. All spectroscopic samples were prepared using spectrographic grade acetonitrile or dichloromethane.

Synthesis of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III), Cr(t-Bu-acac)$_3$. The synthesis of this compound was carried out via modification of a literature preparation.$^{22}$ To a solution of 2 ml water and 2 ml dioxane was added 0.6 g of urea (excess), 0.184 g (1 mmol, 0.208 ml) of 2,2,6,6-tetramethyl-3,5-heptanedione, and 0.089 g (0.33 mmol) of chromium(III) chloride hexahydrate. The reaction was refluxed for 3 days and the product washed with water and recrystallized from benzene/petroleum ether. Anal. Calcd for C$_{33}$H$_{57}$CrO$_6$: C 65.86, H 9.55; found C 65.85, H 9.29%.

Physical measurements

Time-resolved transient absorption data were collected using a one-color femtosecond pump–probe transient absorption instrument in the Beck laboratory that employs the dynamic-absorption approach of Shank and co-workers, where the probe beam is dispersed in a monochromator after passing through the sample.$^{1,4,21}$ The experiments were conducted with 50 fs pump and probe pulses (15 nm FWHM) centered at 600 nm. The detected probe bandpass selected by the monochromator was tuned either to the blue or red of the center of the pump spectrum; data were also acquired using the entire spectrum of the probe beam. Solutions of Cr(acac)$_3$ were prepared with an absorbance of approximately 0.7 at 600 nm in a 1 mm quartz
cuvette. The solution was flowed during the course of the experiment in order to mitigate the effects of thermal lensing. Additional details concerning the experimental procedures, data work-up and fitting to kinetic models are described in the ESI.†

Additional time-resolved absorption data were acquired on Cr(t-Bu-acac)3 using a ~100 fs instrument that has been described previously;24 additional details can be found in the ESI.† Due to limited solubility in CH2Cl2, measurements on this compound were carried out in dichloromethane.25 Sample absorbances were in the range of 0.5–0.7 in a 1 mm pathlength optical cuvette.

DFT calculations were carried out using Gaussian 98 at the UBLYP/6-311G** level, employing a CPCM solvent model for acetonitrile.

The compound of interest in this report is tris(acetylacetonate)-chromium(mnt) (Cr(acac)3). This system was chosen because of its well-documented photophysical properties,28,29 high symmetry, and low quantum yield for photosubstitution (<0.01).30 The relevant low-lying electronic structure of this compound can be understood in terms of (1) the ground state (4A2), arising from single occupancy of each of the three (nominally) t2g-symmetry d-orbitals, (2) (t2g)(eg)-based excited states (4T2 and a higher-energy 4T1 term), and (3) a lower-energy 2E state, corresponding to an intraconfigurational excited state of the 4A2 term. The absorption and emission spectra of this compound are plotted in Fig. 1. Previous work from our group has documented solution-phase ultrafast dynamics associated with formation of the lowest-energy 2E excited state of this compound.24 Following 4A2 → 4T2 excitation in the mid-visible, intersystem crossing (ISC) to the 2E state occurs with a rate constant kISC > 1013 s−1; subsequent vibrational relaxation in the 2E state was inferred from spectral narrowing to occur with a time constant of τVR ~ 1 ps. Variable excitation-wavelength studies further suggested that bluer pump wavelengths resulted in population of higher-lying vibrational levels of 2E, indicating that thermalization within the 4T2 state is not kinetically competitive with ISC. This model was expanded upon through a recent ultrafast IR study by Kunttu and co-workers31,32 who demonstrated that ca. 70–85% of the ground state is recovered via a thermally-induced back-intersystem crossing (BISC) to the quartet manifold (presumably the 4T2 state), which then undergoes internal conversion on a 15 ps timescale to reform the ground state. The remaining 2E population relaxes back to the ground state on a timescale of 760–900 ps, consistent with our previous report.24 The results from both sets of experiments are summarized in the Jablonski diagram shown in Fig. 2. Given that only an upper limit for the time constant for ISC was defined through these experiments (<100 fs), we sought to obtain a more quantitative assessment of this process by enhancing the temporal resolution of the measurement.

Transient absorption data were acquired following irradiation into the 4A2 → 4T2 absorption of Cr(acac)3 at 600 nm. This wavelength corresponds to the low-energy shoulder of the band (Fig. 1): excitation therefore results in the preparation of a (relatively) cool Franck–Condon state on the 4T2 potential energy surface. A positive transient feature was observed, consistent with our previous results showing a net excited-state absorption for the 2E excited state of Cr(acac)3 in the ca. 450–650 nm region.24 A closer examination of the data revealed an oscillation superimposed on this excited-state absorption (Fig. 3). The feature can be described by two components, one having a frequency of 164 ± 20 cm−1 with a damping time constant of τdamp = 70 fs, and a second, much weaker component of 75 ± 25 cm−1 (τdamp = 1.6 ps). This observation is a clear indication of vibrational coherence associated with the photoinduced dynamics of Cr(acac)3.

In recent years, vibrational coherence has been observed in a number of transition metal-based systems: examples include

![Fig. 1](image1.png)  
**Fig. 1** Electronic absorption and emission spectra of Cr(acac)3. The absorption spectrum was acquired in acetonitrile solution, whereas the emission spectrum was obtained at 80 K in a 4 : 1 EtOH/MeOH optical glass. The broad, low-intensity absorption feature centred at 560 nm corresponds to the 4A2 → 4T2 absorption, while emission arises from the lowest-lying 2E excited state.

![Fig. 2](image2.png)  
**Fig. 2** Jablonski diagram summarizing the dynamics of Cr(acac)3 in solution following excitation into the ligand field-state manifold.
Vibrational coherence has been less commonly observed in simple coordination complexes; one of the most compelling recent examples comes from optical studies of [Fe(bpy)₃]²⁺ reported by Chergui and co-workers. In most cases vibrational coherence is associated with a single electronic state, either the initially populated excited state (so-called impulsive absorption) or the ground state (formed via impulsive stimulated Raman scattering). Indirect vibrational coherence mechanisms have also been identified resulting from photochemistry, rapid geometric changes, or formation of some other type of product state. Distinct from these processes is so-called retention of vibrational coherence, wherein a vibrational wavepacket is formed on one electronic surface and propagates through a barrier or avoided crossing to populate another electronic state with the wavepacket still intact. This phenomenon has been observed during internal conversion in cyanine dye molecules, photochemical rearrangements, photoisomerization, and mixed valence species.

The insufficient sensitivity of the instrument to detect modulation by wavepackets on the ground state, as a result of the low oscillator strength of the ground state ligand field absorption, eliminates the possibility that our observation results from vibrational coherence on the ground state surface. However, the excited state absorption, which is charge transfer in nature, provides sufficient oscillator strength to allow one to observe excited state vibrational coherence. This, coupled with the much longer timescales for ground-state recovery (via the ¹T₂ and ³E states as discussed above) strongly implies that the observed vibrational coherence is associated with the excited state(s) of the molecule. Our previous study of this system defined an upper limit for ISC of ca. 100 fs. Given that the oscillatory component in Fig. 3 is evident at time delays past 400 fs, we conclude that the wavepacket initially created in the ¹T₂ state upon excitation persists upon formation of the ³E state, i.e., vibrational coherence is retained during ISC; in this regard it is tempting to view the damping time constant of ~70 fs as being reflective of this surface-crossing event.

Alternatively, vibrational coherence on the ³E surface could result from an indirect mechanism such as the one implicated for [Fe(bpy)₃]²⁺ in which vibrational coherence is associated with the lowest-energy excited state of the molecule (a ¹T₂ ligand-field state). Chergui and co-workers note that the oscillation of 130 cm⁻¹ is likely due to N–Fe–N bending modes which are coherently excited by the impulsive Fe–N elongation that accompanies the transition from a low-spin to a high-spin state in that system. In the case of Cr(acac)₃ one would also expect significant geometric distortions along the Cr–O bonds in the ¹T₂ excited state, however, there are two important distinctions to consider. First, in Cr(acac)₃, it is the initial (as opposed to the final) state that is characterized by an increased equilibrium metal–ligand bond distance: the ³E product state is an intra-configurational term arising from a spin flip within the t₂g orbital set and thus presents an excited-state potential that is essentially nested with respect to the ground-state ⁴A₂ term. Second, the degree of distortion associated with the ¹T₂ term should be significantly smaller than that of the ¹T₂ term of [Fe(bpy)₃]²⁺ due to the difference in valence configuration (i.e., (t₂g)⁴(e_g)² for high-spin Fe₃⁺ versus (t₂g)⁵(e_g)¹ for the ³E state of Cr₃⁺). Given these considerations, the fact that the vibrational coherence appears to be present at or near Δt = 0, and the vibrationally cool nature of the initially prepared state makes retention of vibrational coherence a more compelling mechanistic assignment in the present case.

Retention of vibrational coherence during the ¹T₂ → ³E conversion suggests that the vibrational mode(s) giving rise to the oscillations evident in Fig. 3 define the reaction coordinate for ultrafast ISC in this complex. In terms of identifying these modes, we start with the work of Perkovic and Endicott who implicated low-frequency modes as playing an important role in ³E → ⁴A₂ conversion of Cr(III) complexes. These workers concluded that systems that were sterically constrained along torsional degrees of freedom tended to exhibit slower rates of ISC relative to compounds with greater flexibility. In a non-constrained system, low-frequency modes result in a trigonal distortion of the compound; it can be shown that such a distortion results in extensive mixing of the d orbitals which would facilitate ISC. Limiting motion along these coordinates would amount to the introduction of a barrier along this pathway, thereby slowing the kinetics of surface crossing. Although this model was developed based on data associated

---

**Fig. 3** Top: Single wavelength kinetic trace of Cr(acac)₃ at 592 ± 2 nm following excitation at 600 nm. An underlying increase in excited-state absorbance (τ = 320 fs) was subtracted from the experimental data in the trace shown above in order to more clearly illustrate the oscillatory signal. The solid line corresponds to a fit of the data to two components: see text for further details. Bottom: Sample fits of the data shown in the top panel to oscillations with frequencies of 144 cm⁻¹, 164 cm⁻¹, and 184 cm⁻¹. The level of agreement suggests that the frequency can be considered reasonably well defined with ω₁ = 164 ± 20 cm⁻¹.

---

zinc porphyrins, heme complexes, other metalloproteins, as well as mixed valence compounds. Vibrational coherence has been less commonly observed in simple coordination complexes; one of the most compelling recent examples comes from optical studies of [Fe(bpy)₃]²⁺ reported by Chergui and co-workers. In most cases vibrational coherence is associated with a single electronic state, either the initially populated excited state (so-called impulsive absorption) or the ground state (formed via impulsive stimulated Raman scattering). Indirect vibrational coherence mechanisms have also been identified resulting from photochemistry, rapid geometric changes, or formation of some other type of product state. Distinct from these processes is so-called retention of vibrational coherence, wherein a vibrational wavepacket is formed on one electronic surface and propagates through a barrier or avoided crossing to populate another electronic state with the wavepacket still intact. This phenomenon has been observed during internal conversion in cyanine dye molecules, photochemical rearrangements, photoisomerization, and mixed valence species.

The insufficient sensitivity of the instrument to detect modulation by wavepackets on the ground state, as a result of the low oscillator strength of the ground state ligand field absorption,
with ground-state recovery, it is reasonable to consider a similar reaction coordinate coupling the \( ^1T_2 \) and \( ^2E \) states in the ultrafast ISC of Cr(acac)\(_3\).

In order to gain further insight into the nature of the low-energy vibrational structure of this system, we carried out ground-state DFT frequency calculations on Cr(acac)\(_3\).\(^{41–50}\) Of the several low-frequency modes that were identified from the calculations, two are of particular note: a symmetric breathing mode at 184 cm\(^{-1}\), as well as a torsional “scissor” mode at 256 cm\(^{-1}\). These calculated frequencies are in very good agreement with bands at 188 cm\(^{-1}\) and 254 cm\(^{-1}\) observed in the Raman spectrum of the compound (Fig. S4†). Drawings of these two modes are provided in Fig. 4. It can be seen that both of these ground-state vibrational modes involve displacements of the primary coordination sphere. The potential surface initially accessed upon excitation should be characterized by a smaller vibrational force constant than the ground state due to the interconfigurational nature of the \( ^4T_2 \) term: both of these ground-state vibrational modes are therefore reasonable candidates for the origin of the 164 cm\(^{-1}\) vibrational coherence in Fig. 3.\(^{50}\) Additional vibrational modes were identified at lower energies, nearly all of which, like those shown in Fig. 4, also involve large-amplitude motion of the peripheral methyl groups and/or twisting of the backbone of the acetylacetonate ligand. These observations suggest an experimental probe of the mechanism of ultrafast ISC, namely the use of steric to modulate motion along this proposed reaction coordinate.

As a test of this hypothesis, we carried out ultrafast time-resolved absorption measurements on Cr(t-Bu-acac)\(_3\), where t-Bu-acac is 2,2,6,6-tetramethyl-3,5-heptanedione. This compound essentially replaces the peripheral methyl groups of acac with bulkier tert-butyl groups, thereby increasing the degree of steric interactions associated with the modes depicted in Fig. 4 without significantly affecting the zero-point energies of the electronic states involved in the ISC process. Time-resolved absorption data were acquired on Cr(t-Bu-acac)\(_3\) in fluid solution following excitation on the low energy shoulder of the \( ^4A_2 \rightarrow ^4T_2 \) absorption. The full differential absorption spectra are shown in Fig. 5A, along with data on Cr(acac)\(_3\) that we have previously reported (Fig. 5B).\(^{24}\) The spectral profile for Cr(t-Bu-acac)\(_3\) at the longest time delay shown (\( \tau = 12 \) ps) is invariant out to several hundred ps; this fact coupled with its similarity to the analogous data for Cr(acac)\(_3\) confirm this transient as originating from the \( ^2E \) excited state of the compound. In contrast to the data on Cr(acac)\(_3\), the data on Cr(t-Bu-acac)\(_3\) are characterized by significant changes in the overall profile of the differential absorption spectra at early times. Single-wavelength kinetic traces for Cr(t-Bu-acac)\(_3\) are plotted in Fig. 6. Consistent with the spectral evolution evident in Fig. 5A, data at 450 nm reveal a decay in the excited state absorption, whereas an increase in excited-state absorption is evident at 550 nm. The fitted time constants are slightly different at the two probe wavelengths, but are likely within experimental error (\( \tau \sim 1.8 \pm 0.4 \) ps).

One can envision two distinct models for describing these data: (1) dynamics taking place on a single potential energy surface, which given the data at \( \Delta t = 12 \) ps means vibrational relaxation in the \( ^2E \) state, or (2) dynamics corresponding to a change in electronic structure, in this case conversion from the initially formed \( ^4T_2 \) state to the \( ^2E \). The first model is the one we...
In this context, we note that the qualitative difference in the state at the expense of features characteristic of the initial state. This pronounced intensity; by 12 ps, we observe an absorption band that is identical in all respects to that of Cr(acac)3. This pronounced difference in the nature of the observed spectral changes between the two compounds compels us to ascribe the data on Cr(t-Bu-acac)3 to a direct observation of the \( ^4T_2 \rightarrow ^4E \) conversion in this compound.

To further substantiate this two-state kinetic model, we carried out a Gaussian deconvolution of the differential absorption data of Cr(t-Bu-acac)3. Our analysis presumed the presence of a single absorption band arising from each electronic state. The spectra at long delay times \( (i.e., \Delta \tau > 10 \text{ ps}) \) can be described by a single Gaussian centered at 19 050 cm\(^{-1}\) (525 nm) with a full width at half-maximum (FWHM) of \(~1200 \text{ cm}^{-1}\) \( (2 \text{ ps}) \) is shown in Fig. 7A as an example. Allowing only for changes in the relative areas of the two bands \( (i.e., \text{keeping constant the absorption maxima, band shape, and absorption cross-sections of the two Gaussians}) \), one can easily reproduce the data on Cr(t-Bu-acac)3 (Fig. 7B). At the earliest delay time \( (\Delta \tau = 300 \text{ fs}) \) the integrated signal has roughly equal contributions from both the high-energy and low-energy features; subsequent spectra are characterized by a decay of the band at 465 nm concomitant with the growth of the absorption at 525 nm.

Despite the simplicity of this model, the spectral evolution observed for Cr(t-Bu-acac)3 can clearly be described in terms of a conversion from one absorption profile to another. Specifically, we suggest that the feature near 465 nm in the deconvolved spectra corresponds to absorption(s) associated with the \(^4T_2\) state; the decay of this feature thus reflects depopulation of the \(^4T_2\) state as a result of conversion to the \(^4E\) state of the compound. It should be emphasized that we have no knowledge concerning the relative oscillator strengths of the excited-state absorption features for this compound: we therefore cannot provide a quantitative assessment as to what the relative areas of the deconvolved contributions imply concerning population distributions. Nevertheless, within the context of this model, the observed time constant corresponds to the rate of intersystem crossing. Replacing the peripheral methyl groups in Cr(acac)3 with tert-butyl groups in Cr(t-Bu-acac)3 has therefore decreased the rate of ISC by more than an order of magnitude. While we cannot at this stage be too specific in terms of which normal modes are dominant,\(^{48}\) we believe these results lend considerable credibility to the notion that the sorts of low-frequency vibrational modes discussed above are indeed those driving ultrafast intersystem crossing in this system.\(^{52}\)

Conclusions

The work presented in this report provides compelling evidence that the reaction coordinate of the ultrafast intersystem crossing process in Cr(acac)3 has been identified. Following excitation into the \(^4A_2 \rightarrow ^4T_2\) ligand-field absorption of the compound, vibrational coherence was observed superimposed on the kinetics associated with excited-state evolution. DFT calculations suggested that the 164 cm\(^{-1}\) frequency of the observed oscillations was associated with Cr–O bond stretch vibrations that also involve large amplitude motions of the peripheral methyl groups of the ligand framework. This hypothesis was then tested through the ultrafast spectroscopic characterization of Cr(t-Bu-acac)3, in which the peripheral methyl groups of the acac ligand were replaced by electronically similar but sterically bulkier tert-butyl groups. Time-resolved absorption data on Cr(t-Bu-acac)3 revealed significant changes in the differential
absorption spectrum over the first several picoseconds following \( \text{A}_2 \rightarrow \text{T}_1 \) excitation, indicating that the rate of the \( \text{T}_2 \rightarrow \text{E} \) intersystem crossing had been slowed by more than an order of magnitude relative to \( \text{Cr} \text{(acac)}_3 \). This result is consistent with the magnitude relative to \( \text{Cr} \text{(acac)}_3 \) as a result of this compositional change to the system. We believe that these results constitute a significant step in our ongoing efforts to understand and ultimately control ultrafast excited-state dynamics of transition metal-based systems through the identification of the reaction coordinates associated with photo-induced transformations.

Acknowledgements

The authors would like to thank Prof. C. Reber and Alexandre Rodriguez-Witchel of Université de Montréal for the Raman spectrum of \( \text{Cr} \text{(acac)}_3 \). This work was supported with funds from the National Science Foundation through grant nos. CHE-0911592 (J.K.M.) and MCB-052002 (W.F.B.).

Notes and references