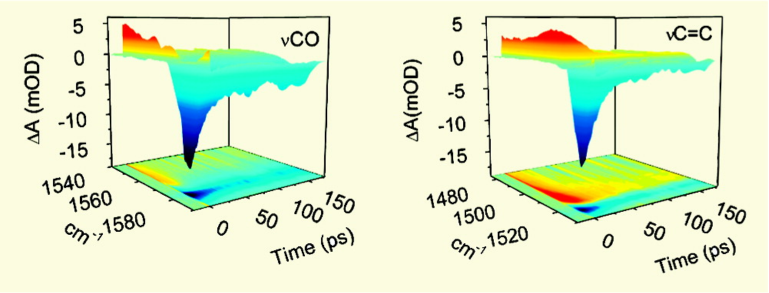
Communication

Relaxation Dynamics of Cr(acac) Probed by Ultrafast Infrared Spectroscopy

Ermelinda M. S. Maas, Robertas Kananavicius, Pasi Myllyperki, Mika Pettersson, and Henrik Kunttu

J. Am. Chem. Soc., **2007**, 129 (29), 8934-8935• DOI: 10.1021/ja071859k • Publication Date (Web): 30 June 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Relaxation Dynamics of $Cr(acac)_3$ Probed by Ultrafast Infrared Spectroscopy

Ermelinda M. S. Maçôas,* Robertas Kananavicius, Pasi Myllyperkiö, Mika Pettersson, and Henrik Kunttu

Nanoscience Center, Department of Chemistry, P.O. Box 35, FI-40014, University of Jyväskylä, Finland

Received March 16, 2007; E-mail: emmacoas@jyu.fi

Photochemistry and photophysics constitute fascinating examples of light-matter interactions with particular importance for our understanding of electronic structure of complex molecules and time scales of elementary chemical events. For obvious technological reasons, such as the demand for new approaches for solar energy conversion, research in inorganic photochemistry has grown particularly strong over the past decades.[1] Investigation of Cr(III) complexes has been of fundamental relevance for the understanding of the photochemistry and photophysics of transition metal complexes.[2]

Cr(III) photochemistry, photophysics, and spectroscopy have been reviewed quite extensively.[3−9] The essentials of the photophysics can be understood in terms of three levels: $^4A_2$,$^4T_2$, and ^2E. One of the central issues has been the role of the quartet and doublet states in Cr(III) photoreactions. In fact, solid evidence exists for reactivity involving both states[8,9] and at two separate time scales: subnanosecond and slower comparable with the long lifetime of ^2E.[10−12] The role of ground state intermediates as well as back-intersystem crossing in the doublet reactivity is still under debate.[5] Since reactivity is ultimately tied to the excited state dynamics, ultrafast pump−probe studies are expected to bring valuable complementary information on the subject.[7,13]

McCusker and co-workers have recently applied femtosecond time-resolved electronic absorption spectroscopy to probe the excited state dynamics of $Cr(acac)_3$ (acac = deprotonated monoanion of acetylacetone) in acetonitrile.[14] $Cr(acac)_3$, which has $^4A_2 \rightarrow {}^4T$ ligand field as well as charge transfer transitions accessible with standard laser sources, is practically nonreactive in aprotic solvents.[15] The transient signal observed upon $^4A_2 \rightarrow {}^4T_2$ excitation was assigned to absorption of the lowest excited doublet (^2E, reported to be ~31 kJ mol^{-1} lower in energy than the $^4T_2$ state).[16] The 1 ps decay of this transient absorption was ascribed to thermalization of the ^2E state.[14] Furthermore, the lack of any time-dependent spectral evolution, within the time resolution of the experiment, was interpreted as an indication of a $^4T_2 \rightarrow {}^2E$ conversion (i.e., prompt intersystem crossing) with rate exceeding 10^{13} s^{-1}. Shorter wavelength excitation of the ^{4}LMCT state yielded an additional 50 fs decay component, which was attributed to direct conversion from the ^{4}LMCT state to the doublet manifold. It should be emphasized that ground state recovery kinetics, as obtained from direct time-resolved experiment, has not been reported in any of the previous investigations. The severe spectral overlap between ground and excited state absorptions prevents the observation of ground state recovery dynamics by transient electronic absorption spectroscopy. Without this information, however, it is not possible to access the relevance of the ^2E state in the photophysics of the $Cr(acac)_3$ complex. The question is whether relaxation via the ^2E state really is a major relaxation pathway for an excess energy initially introduced in the ligand field or in the charge transfer state manifold.

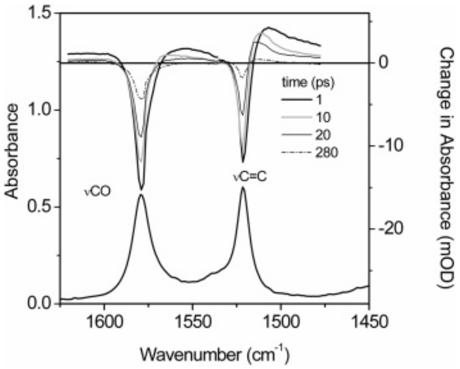


Figure 1. Steady state (lower trace) and transient spectra (upper trace) observed after 400 nm excitation of $Cr(acac)_3$ in TCE.

We have further addressed the dynamics of $Cr(acac)_3$ by transient infrared spectroscopy in room temperature 20 mM tetrachloroethylene (TCE) solution. Due to the narrow bands of vibrational transitions, this is a technique that can potentially provide identification of the absorbing species beyond the capabilities of time-resolved UV−vis absorption spectroscopy. Nibbering et al. have provided an excellent outlook into time-resolved IR spectroscopy.[17] Our goal was to investigate the ground state dynamics upon excitation of the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4$LMCT transitions, at 400 and 345 nm, respectively.[14] TCE provides a transparent window for detection of the strong νCO (≈1579 cm^{-1}) and νC=C (≈1521 cm^{-1}) ground state vibrations of $Cr(acac)_3$.[18] The experiment utilizes the broad (~200 cm^{-1}) spectral width of the short IR pulses as a dispersed light source entering the sample at adjustable delay from the pump pulse. Typical pump energies were 1−2 μJ, and the power dependence of the transient signals was linear. The full spectrum within the IR bandwidth is recorded with a 2 × 64 channel HgCdTe detector. The time resolution is estimated to be 400 fs. Full description of the experimental setup can be found elsewhere.[19]

The overall time-dependent spectral changes within our detection window are shown in Figure 1. At both pump wavelengths, the ground state absorption bands are strongly bleached at zero delay, and new ~30 cm^{-1} broad transient absorption bands appear red shifted from the bleached bands. At increased delays between the pump and probe, the bleached bands regain intensity, whereas the positive transients show significant narrowing, and their maxima move toward higher frequency. At longer times, the ground state IR spectrum fully recovers, and we found no spectral evidence for formation of stable photoproducts. Similar trends were observed at both excitation wavelengths. As an illustration, Figure 2 shows the time evolution of the νC=C ground state bleach in a time window of 0−400 ps. The bleach recovery is clearly composed of two time scales. Double exponential fits of the data yielded a characteristic time of 15 ± 1 ps for the fast component, while the rest of the signal recovers with a time constant of 760−900 ps

10.1021/ja071859k CCC: $37.00

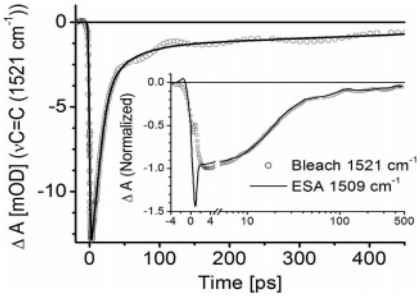


Figure 2. Time evolution of the bleach recovery of the νC=C (1521 cm^{-1}) band of Cr(acac)$_3$ in TCE upon excitation at 400 nm. The solid line represents biphasic fit with time constants $\tau_1 = 15$ ps and $\tau_2 = 760$ ps. The inset shows the correlation between the bleach and the excited state absorption (ESA) at 1509 cm^{-1} (with reversed sign). The sharp feature near zero delay is a coherent artifact.

(this slow component is subject to somewhat larger error). The obtained decay traces show only minor variation with respect to the vibrational mode or pump wavelength. As obvious from Figure 1, the spectral overlap between the negative and positive absorption complicates the analysis of the kinetics, particularly for the νCO, which appears as a broad absorption between two strong bleach bands in a region where a weaker but nonzero bleach signal is expected. This problem can be overcome by a fitting procedure as shown in our previous report on the related Fe(acac)$_3$ complex.[19] The results show that the bleach recover is dominated (70−85%) by the fast process (15 ps). Preliminary measurements undertaken in acetonitrile yielded qualitatively similar results. In this case, the time constant for the fast bleach recovery process is ~10 ps (see Supporting Information). As shown in Figure 2, once the line shape of the transient absorption becomes time-independent ($t > 15$ ps), both bleach recovery and decay of transient absorption signals exhibit the same 760−900 ps time constant. Since this time constant correlates well with the time constant for ^{2}E depopulation (see Supporting Information),[14] we conclude that the main contribution to the transient absorption at later times comes from a vibrational transition of the ^{2}E state.

Our interpretation of the transient data is based on assumption that the behavior of the IR bands is directly related to molecular populations. Thus, the prompt bleach of the two IR bands followed by recovery at later times reflects the full relaxation chain initiated by Franck−Condon access of the vibronic levels of the excited states. Although the vibrational frequencies of the ^{2}E state are predicted to be very similar to the ground state,[3,4] the fact that the bleach recovers with completely identical spectral shape and position suggests that we are directly monitoring repopulation of the vibrational ground state of $^4A_2$. In fact, the spectrum at long delay (>50 ps) shows that the ^{2}E state absorption is distinctly red shifted and broadened compared to the ground state.

The interpretation of previous pump−probe measurements yielded that intersystem crossing (ISC) between the quartets and doublets is ultimately fast and exceeds vibrational relaxation.[14] Then our results suggest that ISC back to the quartet manifold (ground or excited state) takes place within a time scale of about 15 ps. This interpretation is actually in line with the fact that the slow (600−750 ps) relaxation of the ^{2}E state to the ground state is induced by thermally activated ISC as evident from the temperature-dependent luminescence measurements (see Supporting Information). The large excess energy in the system effectively raises the temperature of the molecule after vibrational energy redistribution enhancing the thermally activated ISC to the quartet manifold until vibrational energy relaxation and transfer to the solvent cools the molecule sufficiently to trap the remaining population on the ^{2}E state. Our analysis of the time-dependent line shape gives the vibrational cooling and relaxation time of 7−15 ps. This is significantly longer than deduced from the transient electronic spectroscopy, demonstrating the difference in sensitivity for vibrational dynamics of the different methods.[14a] According to this interpretation, vibrational cooling time is crucial in determining the final populations and, consequently, the quantum yields. Given the widespread range of values for ISC efficiencies reported in different Cr(III) complexes (from 0.2 to 1),[20] the present interpretation is not at odds with the current understanding of Cr(III) photophysics.

In conclusion, the present investigation clearly shows the great value of transient IR spectroscopy in inorganic photophysics. In particular, our results suggest that most (70−85%) of the ground state population of Cr(acac)$_3$ recovers with a time constant of 15 ps, and the rest follows the lifetime of the ^{2}E state. Detailed analysis of the transient absorption line shape dynamics and investigation of vibrational relaxation on the ground electronic state are expected to provide relevant information on the dynamics of bleach recovery. This subject will be addressed in a forthcoming publication.

Acknowledgment. E.M. wishes to acknowledge European Commission for Marie Curie Intra-European Fellowship, and M.P. acknowledges Academy of Finland for financial support.

Supporting Information Available: Arrhenius plot for the temperature-dependent relaxation of the ^{2}E state of Cr(acac)$_3$ in TCE upon excitation at 400 nm; and bleach recovery kinetics and transient spectra upon excitation at 340 nm in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kalyanasundaram, K.; Grätzel, M. *Coord. Chem. Rev.* **1998**, *177*, 347−414. (b) Eisenberg, R.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6799−6801. (c) Armaroli, M.; Balzani, V. *Angew. Chem.* **2007**, *46*, 52−66. (d) Lewis, N. S. *Science* **2007**, *315*, 798−801.
(2) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum Press: New York, 1994.
(3) Forster, L. S. *Chem. Rev.* **1990**, *90*, 331−353.
(4) Kirk, A. D. *Chem. Rev.* **1999**, *99*, 1607−1640.
(5) Irwin, G.; Kirk, A. D. *Coord. Chem. Rev.* **2001**, *211*, 25−43.
(6) Forster, L. S. *Coord. Chem. Rev.* **2002**, *227*, 59−92.
(7) Forster, L. S. *Coord. Chem. Rev.* **2006**, *250*, 2023−2033.
(8) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225−263.
(9) Zinato, E. *Coord. Chem. Rev.* **1994**, *129*, 195−245.
(10) Fukuda, R.; Walters, R. T.; Mache, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097−2103.
(11) Waltz, W. L.; Waters, R. T.; Woods, R. J.; Lilie, J. *Inorg. Chim. Acta* **1980**, *45*, L153−L155.
(12) Waltz, W. L.; Lilie, J.; Lee, S. H. *Inorg. Chem.* **1984**, *23*, 1768−1775.
(13) McCusker, J. K. *Acc. Chem. Res.* **2003**, *36*, 876−887.
(14) (a) Juban, E. A.; McCusker, J. K. *J. Am. Chem. Soc.* **2005**, *127*, 6857−6865. (b) Juban, E. A.; Smeigh, A. L.; Monat, J. E.; McCusker, J. K. *Coord. Chem. Rev.* **2006**, *250*, 1783−1791.
(15) Zinato, E.; Riccieri, P.; Sheridan, P. S. *Inorg. Chem.* **1979**, *18*, 720−724.
(16) Forster, L. S. *Inorg. Chim. Acta* **1998**, *277*, 211−218.
(17) Nibbering, E. T. J.; Fidder, H.; Pines, E. *Annu. Rev. Phys. Chem.* **2005**, *56*, 337−367.
(18) Diaz-Acosta, I.; Baker, J.; Cordes, W.; Pulay, P. *J. Phys. Chem. A* **2001**, *105*, 238−244.
(19) Maçôas, E. M. S.; Kananavicius, R.; Myllyperkiö, P.; Pettersson, M.; Kunttu, H. *J. Phys. Chem. A* **2007**, *111*, 2054−2061.
(20) Bolletta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* **1976**, *80*, 2499−2503.

JA071859K