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Review

Application of transient infrared and near infrared spectroscopy to transition metal complex excited states and intermediates

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Abstract

Transient infrared spectroscopy (or time-resolved infrared spectroscopy, TRIR) on the nanosecond and faster timescales has continued to evolve as a routine and, sometimes, definitive tool both for elucidation of electronic and molecular structures in metal complex excited-states. This review examines examples from the literature since 1998 and discusses experimental methods for performing transient infrared experiments and recent novel applications of TRIR to the excited states of transition metal complexes. While the interrogation of "reporter" ligands such as ν(CO) and ν(CN) modes in metal carbonyl and cyanide complexes and ν(C=O) ligand modes, has grown extensively toward the identification

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of excited states and important features of their bonding, there have been many exciting extensions of the transient infrared technique in recent years. TRIR has been increasingly applied to many types of excited states, resulting in a well-established methodology for assigning excited-state identities. The usefulness of this method has been demonstrated in the unraveling of the sometimes complicated photophysical behavior associated with the complex interplay of multiple excited states, such as closely-spaced MLCT, intra- (IL) and interligand, and dd (ligand-field (LF)) excited states. In recent years, efforts to relate ground-to-excited state vibrational band shifts with other excited state properties (such as the ground-to-excited state energy gap), and medium effects have brought new insights to the understanding of electronic structure in excited states. Application of electronic structure calculations, such as density functional theory approaches, has proven to be a very powerful tool when combined with TRIR in this regard. Relatively new developments, such as non-linear 2D infrared (T2D-IR) spectroscopy, spectroscopic extension into the near infrared, and time-resolved dynamic imaging methods offer exciting possibilities for future applications, and have already presented new capabilities for providing additional insight into the excited states of transition metal complexes.

Keywords: Time-resolved infrared spectroscopy; TRIR; Excited states; Infrared; Transition metal complexes

1. Introduction

One of the most important advances in inorganic spectroscopy over the past 20 years has been the development of time-resolved infrared spectroscopy (TRIR) [1–5]. As applied to transition metal complexes, this technique has been of great assistance in understanding the structures and properties of excited states. It has become an important, often seminal, tool in photochemical and photophysical studies. It has also been effectively applied in other research areas including organic photochemistry, chemical and biological reaction mechanisms, and chemical physics [6].

TRIR has proven to be especially valuable in the study of transition metal complexes containing so-called "reporter" ligands such as CO or CN. Their value in this regard comes from the high oscillator strengths of their stretching vibrations and their π-backbonding relationships with the metal in transition metal complexes. Backbonding makes frequencies and bandwidths of ν(CO) and ν(CN) infrared bands sensitive to changes in electronic and molecular structure. Following metal-based excitation, transient changes occur in these bands on the femtosecond to microsecond timescale. They are often characteristic and can be correlated to changes in electronic structure within the molecule.

More recently, the technique has been applied to ultrafast timescale events, to ring stretching frequencies, and to the near infrared. It has found application in increasingly more complex excited dynamics involving electron transfer, isomerization, and temporal excited-state competitions. The method has also been applied in diverse environments, such as in multiple types of solid matrices and at variable temperatures.

The focus of this review is on recent developments in TRIR (since ~1998) specifically in its application to the excited states of transition metal complexes. Application of TRIR to excited states was initially reviewed in 1993 [7]. A more general review, including application of both TRIR and transient resonance Raman to metal complex excited states, appeared in 1998 [1] and another on TRIR in 1999 [8]. A review in 2000 focused specifically on application of step-scan FTIR in TRIR studies [9].

The emphasis in the early work was on the transient behavior of ν(CO) bands in the 1800–2200 cm^{-1} region. TRIR was used to probe transition metal complex excited states by shifts in reporter ligands, especially ν(CO). The vast majority of studies correlated excited- and ground-state ν(CO) shifts in diimine complexes containing the Os(CO), $Re(CO)_3$, $Re(CO)_2$, and $Ru(CO)_2$ groups having lowest metal-to-ligand charge-transfer (MLCT) excited states. Large, positive ν(CO) shifts were observed characteristic of loss of $d\pi$–π^*(CO) backbonding and strengthening of the CO multiple bond in the excited state.

In particular, early studies focused on complexes containing the $Re(CO)_3$ group because of ease of synthesis and ligand-based "tunability" of excited-state properties. Changes in electron density at the metal in MLCT excited states were inferred from the magnitudes of $\Delta\nu$(CO) shifts with the three ν(CO) normal modes affected differently. Variations in these shifts from complex-to-complex were attributed to the extent of charge transfer to the acceptor ligand.

Electronic origins of excited state(s) were inferred from magnitudes of $\Delta\nu$(CO) shifts. Examples of MLCT, ligand-centered, and $\sigma\pi^*$ excited states were all documented, as well as, examples in which more than one type of state dictated excited-state properties [1].

For complexes containing the $Re(CO)_4$ and $W(CO)_5$ groups, examples were found of lowest ligand-centered excited states and of initial MLCT excited states followed by decay to lower ligand-centered states. Evidence for competing MLCT and XLCT (Halide-to-Ligand Charge Transfer) excited states was found in ruthenium carbonyl halide complexes.

Another area that established the value of TRIR prior to 1998 was use of ν(CO) or ν(CN) shifts to chart excited state intramolecular electron and energy transfer. In multi-site assemblies, application of this technique provided direct evidence concerning the sites involved in excited-state electron or energy transfer. The technique was also applied to non-CO or CN^- containing complexes by monitoring ligand-based bands such as ν(C=O) shifts of carbonyl groups in the fingerprint region, 1650–1400 cm^{-1}.

The focus of this review is on advances, largely in the past six years, of the application of TRIR to transition metal complex excited states. Significant progress has been made during this period through application to new complexes, enhancements in temporal resolution and spectroscopic range, and increasingly sophisticated application of the technique to the unraveling of complex excited-state behavior.