

Rendiconti Accademia Nazionale delle Scienze detta dei XL Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali 138° (2020), Vol. I, fasc. 1, pp. 75-78 ISSN 0392-4130 • ISBN 978-88-98075-38-6

# Role of intersystem crossing in the ultrafast dynamics of optically excited Co(AcAc)<sub>3</sub>

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**Abstract** – In this *rendiconto* we focus on the role of intersystem crossing in optically excited Cobalt tris(acetylacetonate)  $(Co(AcAc)_3)$  in solution. Ultra-fast transient absorption has been exploited to characterize the early stage of evolution of the excited population. The experimental data are compared with the density functional theory calculations. To obtain the geometries and the electronic states of the solvated ion we employed density functional theory, while the excited states and oscillator strengths were provided by the time-dependent density functional theory formalism. The ultrafast rise time of the signal, obtained by the fit of the experimental time evolution, can be associated with intersystem crossing by means of spin-orbit coupling calculated by time-dependent density functional theory. All these considerations suggest that the intersystem crossing efficiently couples the singlet-triplet channels.

Keywords: Chirality; Ultrafast Spectroscopy; Density Functional Theory; Intersystem Crossing

**Riassunto** – In questo rendiconto ci concentriamo sul ruolo dell'"intersystem crossing" nel Cobalto tris(acetilacetonato) (Co(AcAc)<sub>3</sub>) in soluzione, eccitato otticamente. L'assorbimento transiente ultraveloce è stato impiegato per caratterizzare la fase iniziale dell'evoluzione della popolazione eccitata. I dati sperimentali vengono confrontati con i calcoli della teoria del funzionale di densità. Per ottenere le geometrie e gli stati elettronici dello ione solvatato abbiamo impiegato la teoria del funzionale di densità, mentre gli stati eccitati e le forze degli oscillatori sono stati forniti dal formalismo della teoria del funzionale di densità dipendente dal tempo. Il tempo di salita ultraveloce del segnale, ottenuto dall'analisi dell'evoluzione temporale, può essere associato all'"intersystem crossing" per mezzo di un accoppiamento spin-orbita calcolato attraverso la teoria del funzionale di densità dipendente dal tempo. Tutte queste considerazioni suggeriscono che l'"intersystem crossing" accoppi in modo efficiente i canali singoletto-tripletto.

Parole chiave: Chiralità, Spettroscopia Ultraveloce; Teoria del Funzionale Densità; Intersystem Crossing

## INTRODUCTION

The steep rise of the performances of laser sources in terms of time duration of the pulse and repetition rate has paved the road to the development of ultrafast spectroscopies. The pulse durations in the femtosecond and attosecond range has made it possible to perform spectroscopic experiments revealing the de-excitation pathway of the electrons and the role of vibrational motion in the excess energy distribution. Moreover a selected vibrational wavepacket generated by Fourier limited ultrafast pulses provides the possibility of reaction paths that are not accessible on the ground state, widening the field of research of photochemistry [1].

Ultrafast processes may play a key role in the assignment of diffuse interstellar absorption bands in astrochemistry [2] shedding light on the importance of multielectronic excitation and non-Born-Oppenheimer vibronic couplings.

The scenario of dynamics studies following an ultrafast optical excitation could be schematized by the following processes that display a qualitative hierarchy in the time domain. Following the excitation, usually described by the Franck-Condon approximation, there is a relaxation to a lower excited state depicted by three major mechanisms [3]: Vibrational Cooling (VC), which describes the de-excitation from the highest excited to the lower vibrational levels within the same electronic state, Internal Conversion (IC), which provides the deexcitation to a different electronic state within the same spin multiplicity and intersystem crossing (ISC), which stems from a change of the spin quantum number.

Transition metal compounds are of primary importance in the realm of chemical and biological photo-induced reactions [4]. The dynamics of optically excited transition metal compounds [5, 6, 7, 8, 9] revealed the role of ISC in the early evolution of the excited state population.

In this extended abstract we present the study of the role of the intersystem crossing in the dynamics of optically excited Co(AcAc)<sub>3</sub> [10] performed at the EuroFEL Support Laboratory (EFSL) at CNR-ISM.

# EXPERIMENTAL AND CALCULATION METHODS

In this work Co(AcAc)<sub>3</sub> was diluted in acetonitrile (ACN). The geometries and the electronic structures of both the gas phase and the solvated complex, together with their oscillator strengths have been calculated using Density Functional Theory (DFT) and Time Depend-

ent-DFT (TDDFT) formalism coupled with the polarizable continuum model (PCM) based on reaction field calculations and the integral equation formalism. More details about calculations are reported in ref. [10].

The ISC processes have been calculated by means of the non-radiative lifetimes considering spin-orbit coupling matrix elements and the Fermi golden rule with a Franck-Condon weighted density of states (FCWD) [11].

The EFSL facility is equipped with different apparatus devoted to several ultrafast spectroscopy techniques such as Fast Transient Absorption Spectroscopy (FTAS) in transmission and reflection mode in the UV - IR (260-1600 nm) range with temporal resolution of 50 fs, luminescence in up-conversion and single-photon counting with temporal resolution of 50 fs and 200 ps, respectively. An accurate description of the experimental apparatus is reported in ref. [12].

The scientific activity of the laboratory displays interdisciplinary themes such as molecular science [13], metal nano-particle plasmonics [14], nano-structured semiconductors [15], photovoltaic materials [16].

FTAS is a pump-probe experiment based on the detection of difference in absorption or reflectivity between the excited state and the ground state acquired as a function of the delay time after the optical excitation.

#### **RESULTS AND DISCUSSIONS**

The electronic structure of transition metal compounds had been qualitatively, yet effectively, understood by the ligand field approximations. The d shell electron is subjected to a static electron field whose symmetry and intensity mimics the surrounding environment of the ligand molecules.

This approach explains the manifold of electron states present in the optical absorption spectrum by means of d-d transitions and the higher energy features of the spectrum related to ligand to metal charge transfer or metal to ligand charge transfer. In Co(AcAc)<sub>3</sub> the Co ion has d<sup>6</sup> configuration and, according to the ligand field, it has an octahedral splitting: <sup>1</sup>A<sub>1</sub> character is assigned to the ground state, with excited states in order of energy <sup>3</sup>T<sub>1</sub>, <sup>3</sup>T<sub>2</sub>, <sup>1</sup>T<sub>1</sub>. TDDFT theory assign a ligand to metal character to the charge transfer state (LMCT).

The experimental absorption of  $Co(AcAc)_3$  shows a broad peak at 2.1 eV, assigned to d-d transitions of Co and a steep rise starting at 2.4 eV, associated with the LMCT manifold.

From DFT calculations for the gas-phase complex the triplet ground state is the first excited state (about



Fig. 1. Gas phase calculation (upper half of the panel) and ACN solvent calculation (lower half of the panel) of the density of excited states of singlet, triplet, quintet in the geometry of the singlet excited state. Excitation energies are plotted from ref. [10].

1eV above the singlet ground state energy), while the quintet ground state is slightly above the triplet state. For the ACN solvent, the order is reversed and the quintet ground state is the first excited state with energy 0.8 eV above the singlet ground state.

The investigated excitations were at 390 nm (photon energy 3.18 eV) and 365 nm (photon energy 3.40 eV) for the LMCT excited states and 580 nm (2.13 eV) and 650 nm (1.91 eV) for ligand field excited states.

In figures 1 the calculated energy densities of excited states for singlet, triplet and quintet states of Co(AcAc)<sub>3</sub> in the gas phase (two upper panels) and in ACN (two lower panels) are depicted. The energy densities of states are calculated at the geometry of the singlet state, simulating a sudden transition [10]. The data are convoluted with a Gaussian function with a standard deviation of 100 meV. For both calculations the optically excited singlet density of states presents a sizeable overlap or close proximity with those of the triplet and quintet manifolds. In the case of the ACN calculation, the density related to the singlet state at 3.11 eV overlaps that of the triplet manifold at 3.10 eV. Also the quintet state at 3.07 eV is very near and consequently available for fast transitions. For the density of states near the singlet state at 3.29 eV there is a good overlap with a quintet state at

3.30 eV and proceeding toward lower energies there is a triplet state at 3.23 eV. This proves that after the chosen optical excitations relaxation channels for ISC are efficiently available.

Transient absorbance (TA) spectra do not change shape and features after 2 ps time delay, this is a clear indication that the population of the excited state reaches the lowest available excited state.

The comparison between the asymptotic TA spectra and the TDDFT calculations of the absorption spectra of the lowest energy levels of triplet and quintet states provides important information about the population of the states before the molecule recovers to the ground state. Figure 2 reports the theoretical spectra of triplet and quintet lowest states compared with the experimental TA spectrum measured at 3 ps after 390 nm excitation (3.18 eV), with a rigid shift of 300 meV toward lower photon energies. It is worth noticing that the branching ratio between the two most intense triplet transitions is quantitatively comparable with the one obtained from the experimental curve. This spectroscopic assignment clearly reveals that ISC is active in the dynamics with a predominant singlet-triplet transition.

Lifetime analysis of the experimental data reveals an ultrafast rise time of 0.07±0.04 ps and a decay time of



Fig. 2. Co(AcAc)<sub>3</sub> transient absorption spectrum taken at 3 ps after the excitation at 390 nm (3.18 eV) (black line) and the TDDFT calculated absorption in acetonitrile of the lowest level of the triplet (red line) and quintet (green line). The oscillator strengths are convoluted with a Gaussian function with standard deviation of 100 meV. A shift of 300 meV toward lower energy was applied to the theoretical data. Data are plotted from ref. [10].

 $1.5\pm0.3$  ps for the LMCT excitation and a rise time of  $0.07\pm0.04$  ps and a decay time of  $1.8\pm0.3$  ps for the ligand field excitation [10].

From the lifetime calculation it is worth noticing that for the excited states corresponding to the LMCT the ISC lifetime is within the range 0.1 - 1.0 ps, while in the ligand field case is faster and presents values in the range 0.01-0.02 ps [10].

The ISC calculations performed allows us to disentangle the de-excitation pathway of the LMCT states. The lack of an experimental lifetime comparable with the calculated one suggests that the population after the LMCT excitation undergoes a fast IC to the ligand field states and then a fast ISC to triplet states. In the ligand field case the ISC occurs as the primary process.

In both excitations VC should be considered in the early dynamics described by the experimental ultrafast rise.

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