

Quantum Optimal Control of Bond Selective Separation of Ligands from Organometallic Molecules



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- D. Ambrosek, S. Villaume, L. González and C. Daniel, A Multi State-CASPT2 vs. TD-DFT Study of the Electronic Excited States of $\text{RCo}(\text{CO})_4$ ($\text{R}=\text{H}, \text{CH}_3$) Organometallic Complexes. *Chem. Phys. Lett.* **417**, 545-549 (2005).
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Kurzfassung

Ziel der vorliegenden Arbeit ist die Untersuchung des Mechanismus der quanten-optimierten Steuerung selektiver Liganden-Abspaltung am Beispiel der beiden Modellsysteme Tetracarbonylmethylcobalt $\text{CH}_3\text{Co}(\text{CO})_4$ und Tricarbonylcyclopentadienylmangan $\text{CpMn}(\text{CO})_3$.

Die elektronische Struktur von unterschiedlich substituierten Kobaltcarbonylkomplexen ($\text{RCo}(\text{CO})_4$ ($\text{R}=\text{CH}_3, \text{H}$)) in ihrer Gleichgewichts- und asymptotischer Geometrie, letztere beschreibt die Abspaltung des axialen Liganden, wird vergleichend studiert. Aufbauend auf den Ergebnissen zur elektronischen Struktur der Komplexe werden die fünf niedrigsten elektronischen Zustände, der des Grundzustandes, zwei Metall-Sigmabindung-Ladungstransferzustände (MSBCT = Metal-to-sigma-bond charge transfer) und zwei Metall-Ligand-Ladungstransferzustände (MLCT = Metal-to-ligand charge transfer) miteinander korreliert und die zweidimensionalen Potentialenergieflächen dieser Zustände berechnet. Zudem werden quantendynamische Simulationen für beide Komplexe durchgeführt. Dabei wird die Autokorrelationsfunktion für beide Systeme erzeugt und anschließend Fourier-transformiert, mit dem Ziel theoretische Absorptionsspektren zu generieren. Die Molekulardynamik, die für die ungebundenen MSBCT Zustände auftritt, deutet für den Hydridokomplex auf eine reine Abspaltung des Wasserstoffliganden hin während die Dynamik des Methylkobaltkomplexes einen simultanen Bindungsbruch beider axialer Liganden zeigt. Es wird ein pump-dump Kontrollmechanismus angewendet, um die jeweilig mögliche Dissoziation der Liganden CO oder CH_3 vom $\text{CH}_3\text{Co}(\text{CO})_3$ -Komplex zu untersuchen. Hierbei kann ein selektiver Co- CH_3 Bindungsbruch erzielt werden.

Die Theorie der nicht-resonanten Multi-Photonen-Übergänge (NMT = Nonresonant Multiphoton Transitions) auf dem Gebiet der Femtosekundenspektroskopie wird in einem ungestörten Modell präsentiert. Das Ergebnis dieser Herangehensweise ist eine effektive zeitabhängige Schrödinger-Gleichung. Darüberhinaus wird im Rahmen dieser Arbeit die NMT-Theorie erstmalig in die standardmäßige Theorie der optimalen Kontrolle (OCT = Optimal control theory) eingefügt. Für die folgenden Experimente zur kontrollierten Liganden-Abspaltung wird die Organometallverbindung $\text{CpMn}(\text{CO})_3$ als Modellsystem verwendet. Die Erweiterung der NMT-Theorie auf OCT wird am Beispiel des elektronischen 2-Niveau Systems von $\text{CpMn}(\text{CO})_3$ veranschaulicht. Mehrere Fragestellungen zur Steuerung werden anhand von nichtresonanten zwei- und drei-Photonenübergängen beantwortet.

Abstract

Quantum optimal control mechanisms are investigated for the selective metal-ligand dissociation of two organometallic molecules: tetracarbonylmethylcobalt $\text{CH}_3\text{Co}(\text{CO})_4$ and tricarbonylcyclopentadienylmanganese $\text{CpMn}(\text{CO})_3$.

A comparative study of the electronic structure of $\text{RCo}(\text{CO})_4$ ($\text{R} = \text{CH}_3, \text{H}$) complexes at the equilibrium and asymptotic geometry, which describes the dissociation of the axial ligands, is made. From this study, the five lowest-lying electronic states, corresponding to the ground state, two metal-to-sigma-bond charge transfer (MSBCT) states, and two metal-to-ligand charge transfer (MLCT) states are correlated, and the two-dimensional potential energy surfaces for these states are calculated. Quantum dynamic simulations for both complexes are performed. The autocorrelation function is recorded for both systems and is Fourier transformed to obtain theoretical absorption spectra which are discussed. The quantum dynamics occurring on the unbound MSBCT states for the hydrido complex indicate a pure dissociation of the hydrogen ligand whereas the dynamics for the methyl cobalt complex indicate a simultaneous breakage of both axial ligands. A pump-dump type of control mechanism is employed to investigate the possible single CO or CH_3 ligand dissociation from the $\text{CH}_3\text{Co}(\text{CO})_3$ complex. Selective single Co- CH_3 bond dissociation is achieved.

The theory of nonresonant multiphoton transitions (NMT) in the field of femtosecond spectroscopy is presented in a nonperturbative approach. The outcome of this approach is an effective time-dependent Schrödinger equation. Furthermore, the theory of NMT is implemented for the first time into standard optimal control theory (OCT). The organometallic molecule, $\text{CpMn}(\text{CO})_3$, is used as the model system for subsequent control experiments. The extension of NMT to OCT is exemplified using an electronic two-level system of $\text{CpMn}(\text{CO})_3$. Several control tasks are achieved via nonresonant two- and three-photon transitions.

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Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit den angegebenen Hilfsmitteln selbständig angefertigt habe.

Berlin, den 15. Februar 2007