

Laser System Optimization and Investigation into Photodissociative Pathways of $\text{Mn}_2(\text{CO})_{10}$

Part 1: Experimental Theory and Setup

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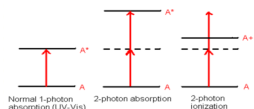
Introduction

Lasers are used as a tool for understanding inorganic molecules and reactivity. In photochemical experiments, laser light is used to break bonds and ionize atoms and molecules by activating electronic excited states. Quantum mechanics gives us the equation:

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{photon}}}$$

The relationship between photon energy and wavelength shows that photons contain discrete amounts of energy, which allow for high selectivity in the processes of bond breakage and ionization. This further proves that energy is quantized, and therefore specific energy levels (such as the desired electronic states) can only be accessed with certain wavelengths. Ultraviolet light of wavelength typically under 400 nm is required to activate these electronic states.

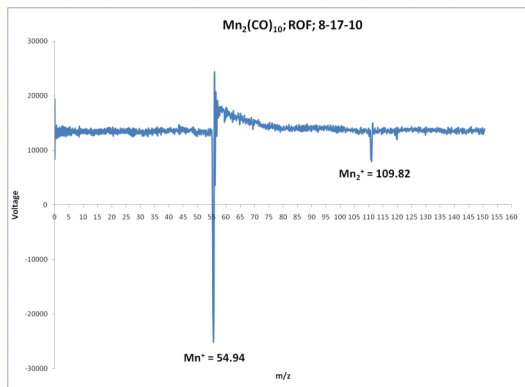
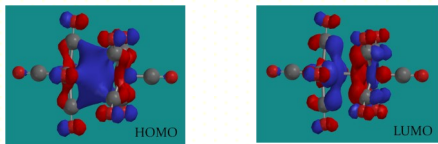
The experiment discussed here examines specifically the photodissociative pathways of dimanganese decacarbonyl in the range of 300-350 nm (see Part 2: Laser System Evolution). We also use multiphoton processes, where laser intensity is high enough that more than one photon is absorbed, to access these higher levels without the use of exorbitantly high energy and to reach energy levels otherwise denied by single photon selection rules.



Possible Dissociation Pathways

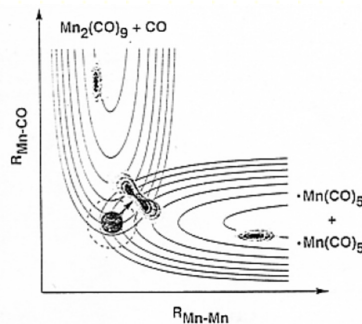
Dimanganese decacarbonyl is said to follow Class B behavior. According to multiphoton ionization and dissociation theories (MPI/MPD)¹, this means that the molecule tends to fragment before ionizing. It relaxes faster than it absorbs a new photon. Because this is a multiphoton process, there is a greater percentage of small ionized fragments due to the ease of accessing high energy levels with additional photons. Most inorganic molecules fall into this category, but it is important to keep in mind that the dissociation classes can change at extremes of laser power, speeds, and wavelength. Class B behavior is indicated by data only exhibiting peaks for small fragments and no detectable parent ion (the completely unfragmented molecule with a positive charge).

The HOMO, or highest occupied molecular orbital, represents the ground state while the LUMO, or lowest un-occupied molecular orbital, which is analogous to the lowest energy excited state. The HOMO and LUMO of $\text{Mn}_2(\text{CO})_{10}$, Spartan calculations shown below, point to metal-metal bond homolysis as the most probable pathway. However, past data often contained a distinctive Mn_2^+ suggesting that the metal-metal bond remained intact. This leaves us with two dominant pathways for dissociation.



Type I Data showing Class B behavior and presence of Mn_2^+ peak.

The two pathways are closely linked and can be described with a potential energy curve, PEC. The diagram² shows the two overlapped pathways, with the ligand loss channel along the y-axis and the metal-metal homolysis along the x-axis. An individual intact parent molecule begins at the height of the contours (the dark circle in the bottom left), and as it moves down it makes the quantum decision to selectively break either the Mn-CO or Mn-Mn bond.



Taking each fragment channel separately, one can see the differences between the two. The Mn-Mn breakage, shown on left below³, requires less energetic photons and the absorption corresponds to and $\sigma \rightarrow \sigma^*$ excitation, while the Mn-CO breakage is higher energy and requires intersystem crossing. Intersystem crossing, a phenomenon where PECs blend together, can only occur for pathways of the same symmetry, which is indicated by the upper case letter describing the curve. For example, there is "A" symmetry for 3A_1 in the PEC for Mn-Mn dissociation.

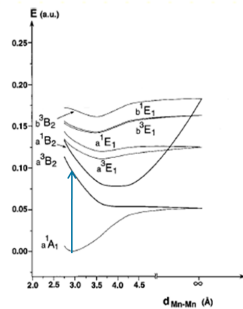


Figure 2. Potential energy curves for the metal-metal bond homolysis in $\text{Mn}_2(\text{CO})_{10}$.

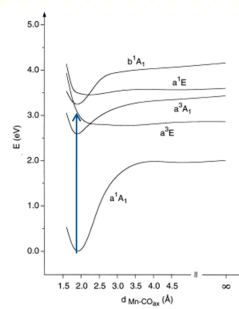
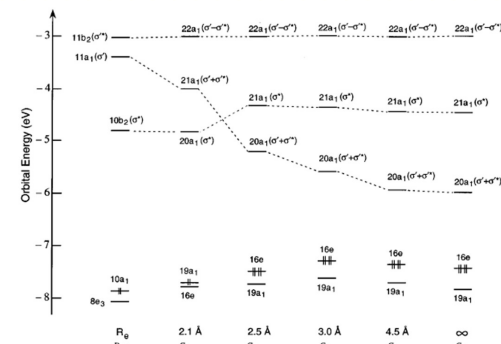
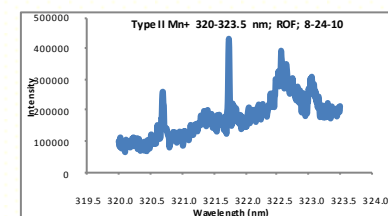


Fig. 5. PECs for the dissociation of the Mn-CO₂ bond in $\text{Mn}_2(\text{CO})_{10}$.

This curve crossing is the factor that allows access to this less-likely ligand loss channel. As the metal-ligand bond stretches out, the overall symmetry of the molecule changes allowing for mixing of the $11a_1$ and $10a_1$ pathways. The ligand loss channel is at lower energy and dissociative when the bond is stretched to 2.5 Å.



This curve crossing is the factor that allows access to this less-likely ligand loss channel. The ligand loss channel is at lower energy and dissociative when the bond is stretched to 2.5 Å. Rosa et al. discusses gas-phase photochemical experiments conducted below 249 nm that show ligand loss channels predominating. Dimanganese decacarbonyl is a widely studied and oft-cited organometallic molecule, though it's primary dissociative pathway upon excitation has not been easily established. Is the theoretical "curve crossing" of the ligand-dissociative channel upon Mn-CO bond lengthening reconcilable with photochemical experiments?



Future Work

□ With these goals in mind, we plan to move into a lower wavelength region and explore predominance of the ligand loss channel in both our current dye and with other dyes using our computer-controlled Type II acquisition method (see Part 2 for details)

to closely monitor both MnCO^+ and Mn_2^+ ion peaks. The sample spectrum above illustrates the important features of the data; the spikes in the Type II data correspond to transitions related to the first photon of the multi-step process. In addition, we hope to confirm peak assignments done by previous researchers for Manganese excited states.

References:

1. A. Gedanken, M. B. Robin, N. A. Kuebler J. Phys. Chem., 1982, 86 (21), 4096-4107.
2. Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. Inorg. Chem. 1996, 35, 2886
3. E.J. Baerends and A. Rosa. Coord. Chem. Rev. 177 (1998), 97

