

Photoionization Mechanisms of Metal Carbonyls with High Power Femtosecond Laser Pulses

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Abstract. High intensity pulses are utilized to explore the photoionization mechanisms involved during femtosecond excitation. A molecular ion signal is observed for both $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ at all wavelengths studied (i.e. 800, 400, and 266 nm). Two distinct ionization mechanisms are proposed. MPI dominates when the multiphoton cross section is large. If the neutral molecules, however, are exposed to sufficient laser intensity barrier suppression ionization occurs. At our highest obtainable powers for 800 nm fs excitation, intact doubly and triply charged molecular ions are observed.

INTRODUCTION

The advent of high power ultra-short pulse laser systems has made it possible to investigate previously unattainable photoionization mechanisms. In "traditional" MPI experiments incorporating ns pulses, a main source of photofragmentation is deactivation of the excited neutral through processes such as internal conversion, intersystem crossing, and electronic or vibrational predissociation. Metal carbonyls have proven to be especially challenging systems when employing ns excitation due to fragmentation prior to ionization through these deactivation channels (1). At all wavelengths studied, the bare metal ion is the dominant species observed in multiphoton ionization experiments (2). It is believed that the main mechanism for photoionization is excitation leading to the stripping of all CO ligands followed by ionization of the central metal. Femtosecond laser pulses, however, are capable of generating absorption rates which may outrun the fragmentation processes which are prevalent in ns excitation of metal carbonyls. In this paper we present results on the photoionization of $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ with femtosecond pulses of 800, 400, and 266 nm light. The molecular ion is observed at all wavelengths for both compounds. Furthermore, intact doubly and triply charged molecular ions are detected with 800 nm light above $2 \times 10^{14} \text{ W/cm}^2$.

EXPERIMENTAL

Photoionization experiments are performed in a reflectron based TOF-MS. Metal carbonyl samples are introduced into the chamber by way of a leak valve. The leak rate is controlled to maintain an operating pressure no greater than 1×10^{-6}

torr to assure collision free measurements. The focused laser beam interacts with the gas-phase molecules in the extraction region of the mass spectrometer. The ionized species are accelerated through a field-free region, travel through the reflecting mirror, traverse a second field-free region, and are finally detected at a dual channel-plate assembly. The reflectron compensates for the initial energy spread introduced by the spatial distribution of the laser beam in the extraction field such that mass resolution of 9000 can be obtained at 200 m/z (3). The laser system used is a Ti:sapphire based regenerative amplified system manufactured by Clark-MXR, Inc. At the fundamental (800 nm), 1.5 mJ 150 fs pulses are generated at 1 kHz repetition rate. The 800 nm light can in turn be doubled and tripled with a LBO and BBO crystal, respectively.

RESULTS AND DISCUSSION

At the high peak powers achieved by focusing the fs laser beam, photoionization mechanisms other than resonant or non-resonant multiphoton ionization become operative. The electric field generated by the laser pulse begins to distort the potential energy surface such that the barrier to ionization is lowered. In turn the probability of tunneling through the coulombic barrier becomes significant. The Keldysh parameter (4,5):

$$\gamma = \omega(2m_e IP)^{1/2} / eE_0, \quad (1)$$

in SI units (where ω is the angular frequency of the laser, IP is the ionization potential, E_0 is the electric field strength, and m_e and e are the mass and charge of the electron, respectively), aids in distinguishing between a MPI and tunneling ionization regime. If $\gamma \gg 1$ then MPI occurs, while at conditions where $\gamma \ll 1$ tunneling ionization is believed to dominate. At even higher laser intensities the coulombic barrier is suppressed such that the electron is no longer bound. The onset for barrier suppression ionization is at the laser intensity (6)

$$I_{(th)} = 4.0 \times 10^9 IP^4 (\text{eV}) / Z^2, \quad (2)$$

where Z is equal to the charge state produced.

As stated above, ns excitation of metal carbonyls leads to the detection of mainly bare metal ions. Whereas with 800 nm fs excitation of Fe(CO)₅ and Cr(CO)₆, shown in Figure 1, intact molecular ions are observed. M refers to the metal core and L denotes the CO ligands. The spectra were taken under identical conditions at an average laser intensity of 8.0×10^{12} W/cm², 200 fs pulses, and at a pressure of 1×10^{-6} torr. The Fe(CO)₅ spectrum exhibits photofragmentation corresponding to consecutive loss of CO ligands, but the molecular ion remains as a prominent peak. The molecular ion, however, is the dominant peak in the Cr(CO)₆ spectrum where very little photofragmentation is observed. The ionization potential for Fe(CO)₅ and Cr(CO)₆ is near 8 eV which corresponds to $\gamma = 2.9$ at these laser conditions. This value suggests that ionization is not through a tunneling mechanism. The threshold value for barrier suppression is 1.6×10^{13} W/cm² for both Fe(CO)₅ and Cr(CO)₆. The reported laser intensities are average

powers, therefore barrier suppression ionization may occur at the peak of the pulse. Possible causes for the differing degree of photofragmentation in the two spectra are ionization through different mechanisms and the lifetime of the neutral intermediate states.

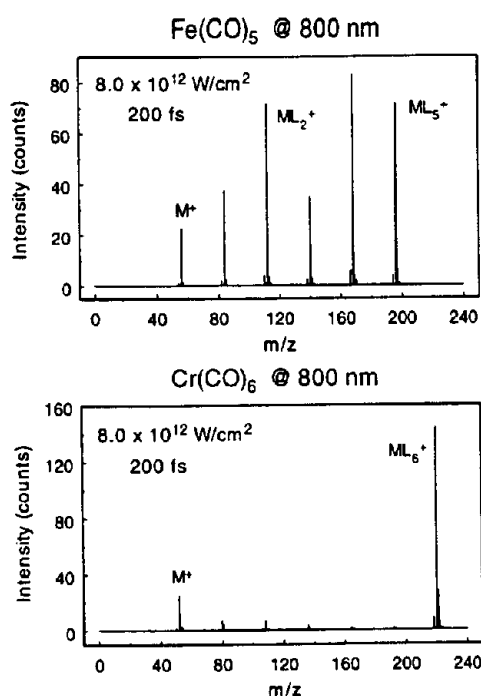


FIGURE 1. Photoionization spectra of Fe(CO)₅ and Cr(CO)₆.

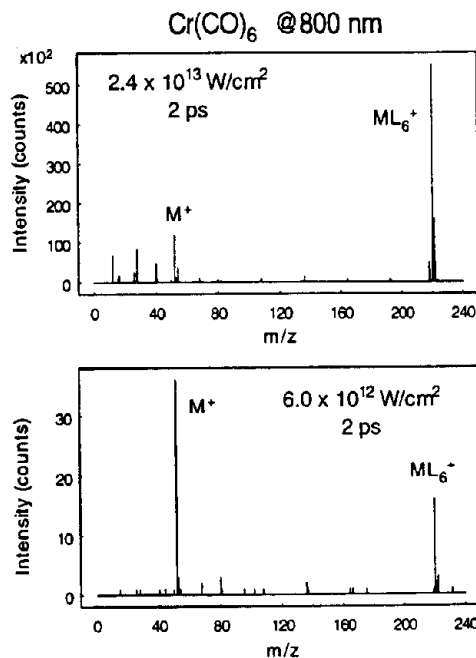


FIGURE 2. Photoionization spectra of Cr(CO)₆ at 800 nm with ps pulses.

To explore the role the lifetime of the neutral excited states plays, we performed photoionization experiments with 2 ps pulses. In the Fe(CO)₅ studies the dominant channel observed at all laser conditions is Fe⁺. Channels corresponding to Fe(CO)_n⁺, where n ≥ 1, comprise less than 25% of the observed peaks, with no species larger than Fe(CO)₃⁺ detected. As shown in Figure 2, however, excitation of Cr(CO)₆ with 800 nm ps pulses exhibits very different behavior. At our highest obtainable peak powers with 2 ps pulses (i.e. 2.4 × 10¹³ W/cm²), the spectrum closely resembles that of fs excitation experiments where the molecular ion is the dominant peak. When the laser intensity is attenuated by a factor of four, an increase in the degree of fragmentation occurs. Photoionization of Cr(CO)₆ with 800 nm light requires six photons. A power dependence study, where the log of the ion counts is measured as a function of the log of the laser intensity over the range 4.0 × 10¹² - 2.4 × 10¹³ W/cm², reveals a slope of 3.8 for the bare metal ion and a slope of 5.4 for the molecular ion channel. This suggests that ionization occurs through two distinct mechanisms. At low laser intensities, the prevailing mechanism is a weak MPI process that leads to the prominent Cr⁺ fragment. As the laser intensity is increased, especially above the threshold value for barrier suppression (i.e. 1.6 × 10¹³ W/cm²), the molecular ion channel begins to dominate. Our data suggest that Cr(CO)₆⁺ arises due to a barrier suppression ionization mechanism. Generation of the molecular ion signal through a MPI process can

not be ruled out, but one would predict a measured photon order closer to that of Cr^+ instead of a totally non-resonant process.

Femtosecond excitation experiments have also been performed at 400 and 266 nm for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$. At both wavelengths for $\text{Fe}(\text{CO})_5$, Figure 3, the molecular ion is the base peak in the spectrum. Photofragmentation channels correspond to consecutive loss of CO ligands. Femtosecond excitation of $\text{Cr}(\text{CO})_6$ at 400 and 266 nm, not shown, exhibits similar results. As the laser intensity increases, for both systems and at both wavelengths, the degree of fragmentation increases. This trend is observed with 800 nm fs excitation also, but an interesting result occurs at our highest obtainable laser intensities. Intact multiply charged molecular ions are detected.

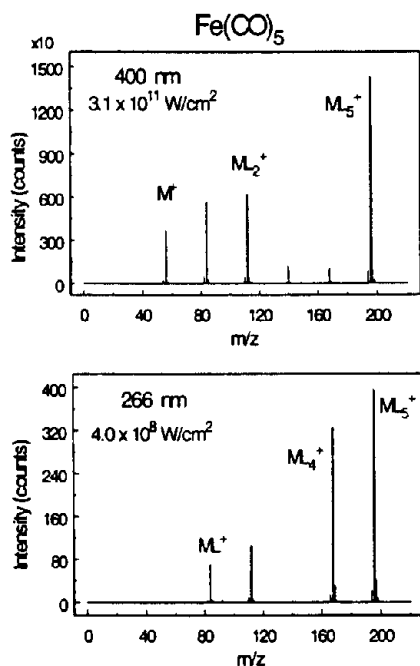


FIGURE 3. Photoionization spectra of $\text{Fe}(\text{CO})_5$ at 400 and 266 nm.

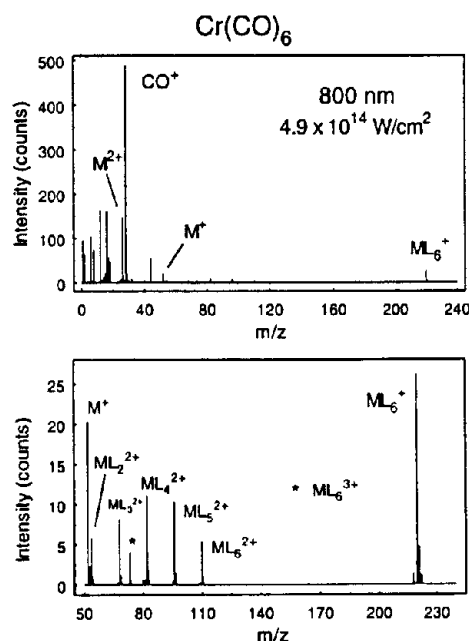


FIGURE 4. Photoionization spectrum of $\text{Cr}(\text{CO})_6$ at peak power of fs excitation.

As can be seen in Figure 4, even at these powers the molecular ion channel is observed for photoionization of $\text{Cr}(\text{CO})_6$. The lower trace in Figure 4 is an expansion of the range from 50 to 240 m/z. The ML_6^{2+} channel is clearly visible with photofragment channels corresponding to the loss of CO ligands. The triply charged molecular ion is also detected and is labeled with an asterisk. One would predict multiply charged molecules of this size to be unstable and undergo Coulomb explosion if the charges are localized on different ligands and the metal. No peak broadening is observed in the mass spectrum as the laser intensity is increased which would rule out an explosion process following ionization. Bonding in the metal carbonyl systems is governed by electrostatics upon ionization. Therefore, if the charge builds on the metal core the CO ligands become more strongly bound to the metal ion due to ion-dipole and ion induced-dipole interactions.

CONCLUSIONS

Unlike ns MPI experiments, we observe molecular ion signal with fs excitation at all wavelengths studied. Two distinct photoionization mechanisms are proposed. For the Fe(CO)₅ system where the MPI cross section is high, ionization occurs before the neutral molecules can be exposed to the peak power of the laser pulse. However, the multiphoton cross section for 800 nm excitation of Cr(CO)₆ is low, thus molecules can be photoionized through a barrier suppression mechanism. With fs excitation at 800 nm intact doubly and triply charged molecular ions are detected above 2×10^{14} W/cm². This observation suggests that the multiple charges may be localized on the metal core. We are currently exploring other systems to determine if this observation is specific for metal carbonyls or is a general phenomena seen for all metal-ligand systems.

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