

Photoionization mechanisms for $\text{Cr}(\text{CO})_6$ using high intensity laser pulses in the near-IR

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Abstract

High intensity (i.e. 10^{13} W/cm²) picosecond and femtosecond laser pulses are utilized to study possible photoionization mechanisms of $\text{Cr}(\text{CO})_6$. This work represents the first example of excitation of a metal carbonyl with 800 nm photons where the ionization of intact molecular species dominates photofragmentation channels. With picosecond pulse excitation, however, attenuation of the laser power appears to induce a higher degree of fragmentation. The data can best be interpreted assuming two distinct photoionization mechanisms where MPI dominates at low laser powers and a transition occurs to barrier suppression ionization as the laser power is increased.

1. Introduction

The photophysics associated with the interaction of ultra-short laser pulses with molecules is an expanding area of research. Here we examine the behavior of $\text{Cr}(\text{CO})_6$ after interaction with 800 nm pulses of 200 fs and 2 ps in duration. This system has proven challenging when using nanosecond excitation. The pioneering work on the photoionization of metal carbonyls by Smalley and coworkers [1] in the late '70s with nanosecond pulses in the 280 nm region for $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, and $\text{Mo}(\text{CO})_6$ led to the detection of predominately bare metal ions even near threshold laser intensities. Absorption in this region corresponds to the excitation of a charge-transfer state [2] which is believed to be strongly predissociative due to its diffuse spectrum. Smalley and coworkers report that ionization efficiencies for the metal ions approach unity even at moderate laser powers (i.e. 10^8 W/cm²). Similar results have been obtained using ns pulses which incorporated other

wavelengths in the UV and the visible [3]. It is believed that the dominant mechanism for the photoionization of these species with nanosecond pulses is the absorption of multiple photons leading to the sequential, rather than concerted, loss of CO ligands followed by ionization of the bare central metal. However, small quantities of $\text{M}(\text{CO})_n^+$ ($\text{M} = \text{metal}$) where $n \geq 1$ have been detected which implies other ionization mechanisms must be operative [3].

Photofragmentation in MPI experiments employing nanosecond pulses has been attributed mainly to deactivation of the excited neutral or ladder switching. Ladder switching [4] corresponds to the absorption of additional photons once the molecule has been ionized which then leads to fragmentation. In turn, fragment ions may absorb additional photons from the laser pulse and undergo further fragmentation. Deactivation of neutral excited states is caused by processes such as internal conversion, intersystem crossing, radiative decay, and electronic or vibrational predissociation which compete with absorp-

tion. Advances in laser technology have produced high power laser systems with pulses in the picosecond and femtosecond regime. These laser pulses are capable of generating absorption rates that can outrun the fragmentation processes which are prevalent in nanosecond excitation of metal carbonyls.

At low laser intensities, where the potential surface is not significantly altered, ionization is governed by multiphoton excitation which can be described using perturbation theory [5]. At high laser intensities, however, the electric field strength generated by the laser pulse approaches the binding strength of a valence electron bound to an atom or molecule. A semi-quantum mechanical approach gives a better description at these laser intensities where the barrier to ionization is sufficiently suppressed such that the probability of an electron tunneling through the barrier becomes significant [6]. At even higher intensities, ionization is best described by an approach where the barrier is suppressed to the point that the electron is no longer bound [7]. In this letter we present results of photoionization experiments on $\text{Cr}(\text{CO})_6$ with high power picosecond and femtosecond pulses in the near-IR. At high laser intensities (i.e. 10^{13} W/cm^2) the molecular ion is the predominant peak in the mass spectrum. When employing picosecond pulses, however, the ratio of fragment to molecular ion signal increases as the laser power is attenuated. We suggest this observation indicates that ionization is governed by a MPI process at low laser intensities, while barrier suppression ionization dominates at high intensities.

2. Experimental

Gas-phase photoionization experiments were performed in a reflectron based TOF-MS manufactured by Kratos, Inc. A detailed description of this apparatus has previously been published [8–10]. The sample is introduced into the mass spectrometer chamber by way of a leak valve to obtain a pressure of 1×10^{-6} Torr during experiments. Photoionization is achieved with pulses generated by a Ti:sapphire based regenerative amplified system manufactured by Clark-MXR, Inc. [11–13]. The Ti:sapphire oscillator lases near 800 nm and is self-mode locking at 100 MHz producing 100 fs pulses with an output

power of $\approx 4 \text{ nJ/pulse}$. Pulses from the near TEM_{00} mode beam are temporally stretched to $\approx 300 \text{ ps}$ by multiple passes on a single grating. These pulses seed the Ti:sapphire regenerative amplifier which amplifies a single pulse from the nJ range to 1.8 mJ/pulse. The pulses are finally compressed back to the femtosecond regime by a grating pair assembly. The laser system is capable of generating 140 fs pulses at 1.45 mJ/pulse and operates at a repetition rate of 1 kHz. Picosecond pulses are generated by reconfiguring the compressor such that the pulses are incompletely compressed. The pulses are no longer transform limited, but remain spatially chirped.

The laser beam is focused in the chamber with a 30 cm MgF_2 lens mounted on an exterior x, y, z translational stage. The output power of the laser is controlled by rotating a half-wave plate which is positioned before the compressor. This operation governs the percentage of light that is reflected from the gratings which in turn determines the final output power. The focused laser beam intercepts gas-phase molecules between the sample stage, biased at 2.7 kV, and an extraction plate located approximately 1 cm above the stage. With this plate grounded, ions are extracted into the field-free region of the time-of-flight mass spectrometer, travel through the reflectron, traverse a second field-free region, and finally are detected with a dual channel plate assembly. We currently employ a multi-hit time-to-digital detection system with 10 ns time resolution.

3. Results and discussion

As stated previously, photoionization experiments of metal carbonyls using ns laser pulses lead to the detection of mainly bare metal ions. One of the dominant mechanisms of ionization for these species is initial excitation which leads to the stripping of all ligands, followed by the ionization of the metal core [3]. With fs excitation, however, the absorption rate should begin to compete with the dissociation timescale of excited neutrals such that ionization suppresses intermediate state fragmentation. As seen in Fig. 1, photoionization of $\text{Cr}(\text{CO})_6$ at a pressure of 1×10^{-6} Torr with 800 nm light and a pulse duration of 200 fs results in a mass spectrum where the predominant peak corresponds to the molecular ion.

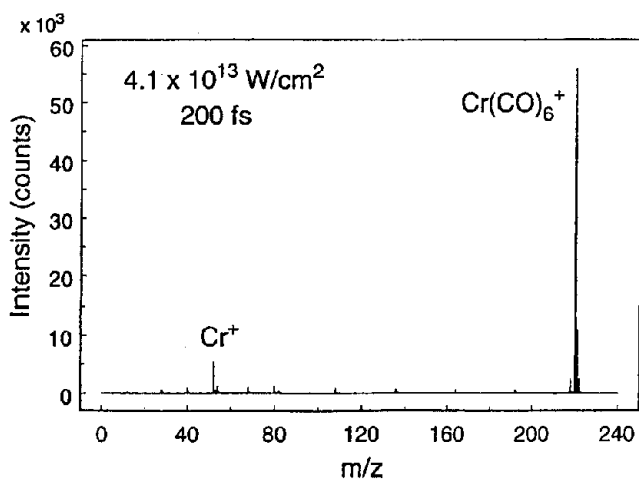


Fig. 1. The photoionization mass spectrum of Cr(CO)_6 using 800 nm, 200 fs pulse excitation. The laser beam is focused to a 100 mm diameter spot which generates a laser intensity of $4.1 \times 10^{13} \text{ W/cm}^2$. The spectrum is an average of 50000 laser shots.

Attenuation of the laser power by more than an order of magnitude produces no change in the spectral profile, only a reduction in counts. This is a significant result when considering the extensive fragmentation observed in the ns photoionization data.

To explore the role that the lifetime of the neutral intermediate states plays in the ionization process, we performed picosecond excitation experiments. Photoionization of Cr(CO)_6 with 800 nm 2 ps pulses, Fig. 2a, generates a similar mass spectrum to that obtained with fs excitation. The degree of fragmentation is slightly greater, but the molecular ion remains the dominant peak. Interestingly though, attenuation of the laser power appears to induce relatively more fragmentation. The mass spectrum in Fig. 2b was taken under identical conditions to that of Fig. 2a except the laser power was attenuated by a factor of four. The bare Cr metal ion is now the largest peak in the spectrum, but still a significant percentage of Cr(CO)_6^+ is detected.

To gain insight into the possible ionization mechanisms that give rise to this intriguing result, power dependence studies were undertaken. If ionization is governed by a multiphoton process, a plot of $\log(\text{counts})$ as a function of $\log(\text{laser intensity})$ will exhibit a straight line with a slope corresponding to the photon order. The ionization potential of Cr(CO)_6 is 8.14 eV [14], thus six 800 nm photons are required to reach the ionization continuum. If the excitation process involves resonant steps, the measured photon

order may be lower. The slopes of the Cr^+ and Cr(CO)_6^+ channels are 3.8 and 5.4, respectively. As seen in Fig. 3, the photon order is clearly different for the two channels, which suggest the signal is derived from dissimilar ionization mechanisms. It is evident from the power dependence study that generation of the molecular ion has not reached a saturation point (i.e. plateau and eventual decrease in counts as the laser intensity increases) where ionic fragmentation channels become prevalent. This regime may be realized at higher ps laser intensities which we are unable to produce at this time.

Previous nanosecond photoionization experiments of metal carbonyls were performed at laser intensities of $\leq 10^9 \text{ W/cm}^2$ where ionization occurred through a resonant or non-resonant multiphoton process. At intensities of 10^{12} W/cm^2 (achieved by focusing a ps or fs laser beam) ac-Stark effects become important, where resonances shift and broaden [15]. The electric field generated by the laser

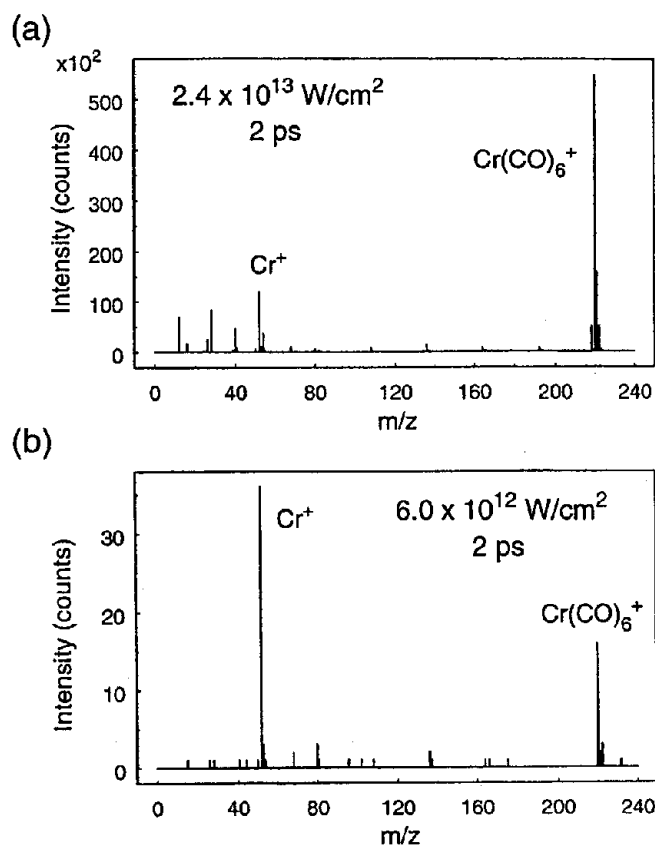


Fig. 2. A comparison of the photoionization of Cr(CO)_6 when incorporating 800 nm, 2 ps pulse excitation at a laser intensity of $2.4 \times 10^{13} \text{ W/cm}^2$ (a) and at $6.0 \times 10^{12} \text{ W/cm}^2$ (b). The mass spectra were recorded under identical conditions of 50000 laser shots and at a focused beam diameter of 40 mm.

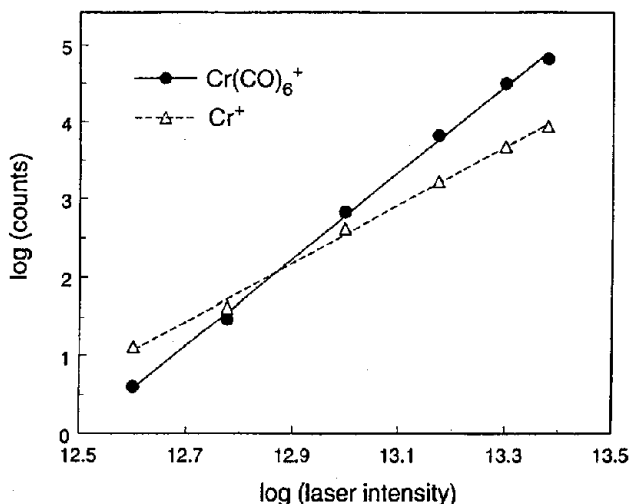


Fig. 3. A plot of the logarithm of the integrated ion intensity in counts as a function of the logarithm of the laser intensity for 800 nm, 2 ps excitation. The dashed line corresponds to the Cr⁺ channel which has a measured slope of 3.8, while the solid line corresponds to the Cr(CO)₆⁺ channel with a slope of 5.4.

also distorts the potential surface such that the barrier to ionization is suppressed. As a result, at increasingly higher intensities the probability of an electron tunneling through the saddle point becomes greater. Keldysh defined a unitless parameter γ to distinguish between a MPI and a tunneling ionization (TI) regime [16,17]:

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

in SI units, where ω is the angular frequency of the laser, IP is the ionization potential, E_0 is the electric field strength of the laser radiation, and m_e and e are the mass and charge of the electron, respectively. If $\gamma \gg 1$ then MPI occurs, while under conditions where $\gamma < 1$ TI is believed to dominate.

At slightly higher field strengths, the barrier is sufficiently suppressed such that the electron is free to escape. This process, known as barrier suppression ionization (BSI), is described as a valence electron bound by a one-dimensional Coulombic potential where the critical laser intensity required for an electron to escape without tunneling through the barrier is given by the threshold value [18]

$$I_{\text{th}} (\text{W/cm}^2) = 4.00 \times 10^9 \text{IP}^4 (\text{eV}) / Z^2, \quad (2)$$

where Z represents the charge on the ion produced. Unlike TI where the ionization probability changes as a function of laser intensity, BSI occurs only when $I > I_{\text{th}}$ and not below this value. The barrier

suppression model has shown excellent agreement in photoionization experiments of the noble gases over a wide range of charge states [18,19]. Furthermore, the tunneling model has been successfully incorporated in characterizing possible ionization regimes for atoms [7] and molecules [20,21] when employing high intensity excitation.

When performing experiments at high laser intensities, where resonances broaden and shift due to Stark effects, it is not only important to consider multi-order perturbation theory, but also alternative ionization mechanisms. Photoionization data generated with high power femtosecond pulses for polyatomic systems is limited [8,22–26]. Therefore, we have employed the tunneling and barrier suppression model to compare with previous atomic and diatomic results as well as to aid in distinguishing probable ionization mechanisms.

Even though Cr(CO)₆ has many possible ionization channels we detect only two dominate species — Cr⁺ and Cr(CO)₆⁺. In a multiphoton ionization model the molecular ion signal would be generated by direct ionization of Cr(CO)₆ as a result of six photon absorption. A competing ionization channel would be the dissociation of Cr(CO)₆ followed by ionization of the fragments. Due to the bonding nature of Cr(CO)₆ [27,28], a minimum of four 800 nm photons are required to completely strip the CO ligands from the molecule followed by five photon excitation to produce the Cr⁺ channel which is observed. The Cr ion signal may also be produced by an ion dissociation channel (i.e. Cr(CO)₆⁺ + $n h\nu$ → 6 CO + Cr⁺), but we have ruled this out as a dominate channel due to the low CO⁺ signal in the spectra and the non-saturating nature of the power dependence curves in Fig. 3.

When incorporating 200 fs pulse excitation, the absorption rate competes with dissociation processes such that the molecular configuration is preserved upon ionization. At low intensities for 2 ps excitation, Fig. 2b, photofragmentation of Cr(CO)₆ followed by ionization of the bare Cr atom is the dominant channel. Considering this process requires more than six photons and the measured photon order for this channel is 3.8, resonant excitation is involved. At low laser power direct ionization of Cr(CO)₆ by a completely non-resonant process (as suggested by the power dependence curve) would be

inefficient. As the laser intensity is increased, absorption rates compete more successfully with dissociation processes such that neutral photofragmentation channels may be minimized. If this were the explanation for the experimental observations when using 2 ps excitation (i.e. shift in dominance from the Cr^+ channel to that of the molecular ion), one may expect significant intermediate dissociation-ionization channels to be detected as the laser power is increased. However, no intermediate channels corresponding to $\text{Cr}(\text{CO})_n^+$, where $0 < n < 6$, are observed greater than 15% of the Cr^+ signal at any laser intensity.

At the laser intensities incorporated in these experiments, tunneling and/or barrier suppression ionization mechanisms may become operative. Tunneling ionization generally coincides with low frequency excitation in strong laser fields. However, in the near-IR region a transition from a MPI to a barrier suppression mechanism occurs prior to tunneling for atoms with an ionization potential less than 20 eV [7]. The literature on polyatomic systems in strong laser fields is limited, but clearly the interaction between the laser induced electric field and a molecule is different from that with an atom. Experimentally we are unable to distinguish between a molecular tunneling mechanism and barrier suppression, however, from a wavelength argument BSI is more probable. The laser intensities used to generate the mass spectrum in Fig. 1 (i.e. $4.1 \times 10^{13} \text{ W/cm}^2$) and Fig. 2a (i.e. $2.4 \times 10^{13} \text{ W/cm}^2$) are above the threshold value of $1.8 \times 10^{13} \text{ W/cm}^2$ for BSI of $\text{Cr}(\text{CO})_6$. As stated above, multiphoton excitation with femtosecond pulses is expected to preserve molecular information. Therefore, it may be difficult to observe a clear transition from a MPI to a barrier suppression regime considering the ion products would be similar. This would account for our result when incorporating fs excitation where the spectral profile remains constant over an order of magnitude change in laser intensity. Ion fragmentation channels may become prevalent at higher intensities, but they are minimal at $4.1 \times 10^{13} \text{ W/cm}^2$. In ps pulse experiments at low laser intensities, Fig. 2b, a weak MPI process dominates which leads to ligand stripping followed by ionization of the bare Cr atom. This result is reminiscent of ns excitation experiments where intermediate photofragmentation chan-

nels prevail. As the laser intensity is increased above the BSI threshold value, Fig. 2a, a barrier suppression mechanism dominates generating the molecular ion signal. As discussed above, a MPI process should generate intermediate channels as the laser power is increased rather than the abrupt change which is observed from a Cr^+ to an intact molecular ion.

4. Conclusion

In summary, we have identified two distinct ionization regimes for $\text{Cr}(\text{CO})_6$ when employing picosecond and femtosecond excitation. It is evident that within a high intensity laser pulse multiple ionization mechanisms become operative. Future photoionization experiments will entail power dependence studies for fs excitation as well as exploration of the photophysics involved during excitation with higher intensity pulses (i.e. 10^{14} W/cm^2). Additional metal carbonyls are also being examined to investigate if the intriguing results obtained here are unique to this system or are general for a class of compounds.

Acknowledgements

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