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# RESONANCE IONIZATION SPECTROSCOPY

Ninth International Symposium

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Manchester, United Kingdom June 1998

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John C. Vickerman

*The University of Manchester  
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**Woodbury, New York**

# Femtosecond Photodissociation Dynamics of $\text{Cr}(\text{CO})_6$

T. Kono<sup>1,2</sup>, V. Vorsa<sup>1</sup>, K. F. Willey<sup>3</sup>, N. Winograd<sup>1</sup>

<sup>1</sup>Department of Chemistry, The Pennsylvania State University  
184 Materials Research Institute Building, University Park, PA 16802, USA

<sup>2</sup>Permanent address ; Analytical Research Laboratory, Asahi Chemical Industry Co., Ltd.  
2-1 Samejima, Fuji-city, Shizuoka 416, Japan

<sup>3</sup>Atom Sciences, Inc.  
114 Ridgeway Center, Oak Ridge, Tennessee 37830-8810 USA

**Abstract.** Pump-probe techniques are used in conjunction with time-of-flight mass spectrometry to investigate the ultrafast photodissociation dynamics of  $\text{Cr}(\text{CO})_6$  following excitation at 200 nm and 267 nm. Time-resolved experiments reveal the first loss of CO ligand(s) occurs within 140 fs.

## INTRODUCTION

Metal carbonyls exhibit unique photochemical behavior that is fundamentally different from small organic and inorganic molecules (1). Photoexcitation of metal carbonyls results in dissociations of multiple bonds, while small inorganic and organic molecules typically exhibit rupture of one bond. This is attributed to the lower bonding energies in metal carbonyls. Beginning with the studies of  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{Mo}(\text{CO})_6$  (2), photoionization of metal carbonyls with nanosecond (ns) laser pulses in the ultraviolet have predominantly resulted in the production of bare metal ions. Several mechanisms for photodissociation have been proposed (1), although the operative mechanism(s) is still under debate.

The rapidly expanding field of femtosecond chemistry is emerging as an ideal forum for the study of the early time behavior of chemical processes (3, 4). Several groups have recently reported time-resolved studies on the ultrafast photodissociation of metal carbonyls in the gas phase. In this study, the researchers probed the real-time dissociation of  $\text{Fe}(\text{CO})_5$  (5) and  $\text{Mn}_2(\text{CO})_{10}$  (6). Previously, our laboratory has investigated the photoionization mechanisms for  $\text{Cr}(\text{CO})_6$  using high intensity laser pulses in the near-IR in which it was proposed that ionization occurs via a barrier suppression mechanism (7). In this paper we describe the ultrafast photodissociation dynamics of  $\text{Cr}(\text{CO})_6$  following excitation at 200 nm and 267 nm.

CP454, *Resonance Ionization Spectroscopy*  
edited by J. C. Vickerman, I. Lyon, N. P. Lockyer, and J. E. Parks  
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## EXPERIMENTAL METHOD

The experiments are performed by coupling a reflectron-based time-of-flight (TOF) mass spectrometer with a femtosecond Ti:sapphire laser system. A variable leak valve introduces  $\text{Cr}(\text{CO})_6$  into the extraction region of the mass spectrometer where it intersects the laser beams and is pulse-extracted into the mass spectrometer. The 1 kHz Ti:sapphire femtosecond laser system (3,7) (Clark-MXR, Inc.) produces 100 fs pulses at 800 nm containing 3.5 mJ of energy per pulse. This output is directed into a harmonic generator to produce 400, 267, and 200 nm wavelengths. The pulse widths for these wavelengths are  $\sim 200$ , 250, and 400 fs, respectively. In the pump probe experiment, the power of pump and probe beam are attenuated so that each pulse yields no significant ion signal. These laser intensities are  $1.8 \times 10^9$ ,  $2.9 \times 10^{12}$ ,  $2.8 \times 10^{11}$  and  $7.9 \times 10^{11}$  W/cm<sup>2</sup> for 267, 800, 200, 400 nm, respectively.

## RESULTS AND DISCUSSION

Single-color, single-pulse photoionization of  $\text{Cr}(\text{CO})_6$  with femtosecond laser pulses at 400 nm, 267 nm and 200 nm are shown in Fig. 1. At threshold laser intensities, 400 nm and 267 nm excitation yield only the molecular ion, while 200 nm excitation produces predominantly  $\text{Cr}(\text{CO})_3^+$  and  $\text{Cr}(\text{CO})_2^+$ . This is because 2 photons of 267 nm and 3 photons of 400 nm excites  $\text{Cr}(\text{CO})_6$  to an energy just above that of  $\text{Cr}(\text{CO})_6^+$ , whereas 2 photons of 200 nm excites it to above threshold energy for  $\text{Cr}(\text{CO})_2^+$  (refer to Fig. 1 (d)). At higher laser intensities, additional photons are absorbed leading to further fragmentation. Since the calculated Keldysh parameter is much greater than 1 for the laser intensities used here, the ions are most likely generated through a multiphoton ionization (MPI) mechanism. These results imply that  $\text{Cr}(\text{CO})_6$  dissociates on the fs time scale.

Shown in Fig. 2 are the ion yields for all species obtained with 267 nm (pump) and 800 nm (probe) pulses (parallel polarization). The 267 nm pump pulse excites the  $^1A_{1g} \rightarrow c^1T_{1u}$  transition. Since 267 nm (4.65 eV) excitation can only dissociate a maximum of 4 M-L bonds, the strong  $\text{Cr}(\text{CO})^+$  and  $\text{Cr}^+$  signals are indicative of fragmentation from the probe pulse. The normalized data (dots in Fig. 3) clearly illustrate the unique fs scale time-dependent behavior of fragment ions following excitation at 267 nm.

In order to explain these results, we attempted a simulation incorporating fragmentation from the probe pulse. We examined several models including a concerted process and one that consists of 2 relaxation scales where the 2nd relaxation occurs from each state in the 1st sequential process. The best fit is obtained with a model incorporating 7 states where each state except the last one relaxes sequentially. The agreement between simulation and experiment is illustrated in Fig. 3. The lifetimes of these initial and intermediate states are 20, 20, 25, 25, 30,

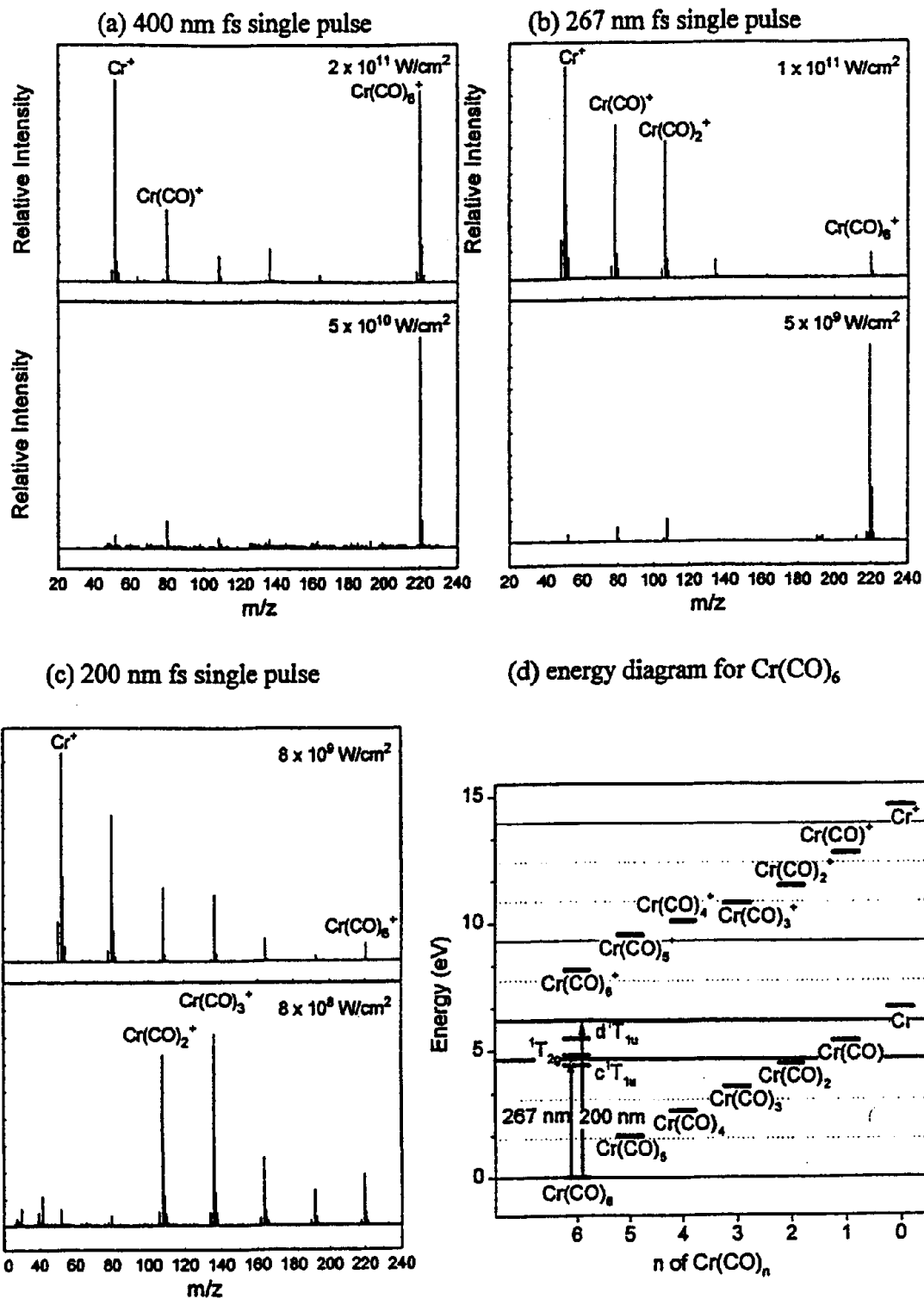


Figure 1. Femtosecond Photoionization Spectra of  $\text{Cr(CO)}_6$  at (a) 400 nm, (b) 267 nm and (c) 200 nm and (d) energy diagram for  $\text{Cr(CO)}_6$  and its fragments.

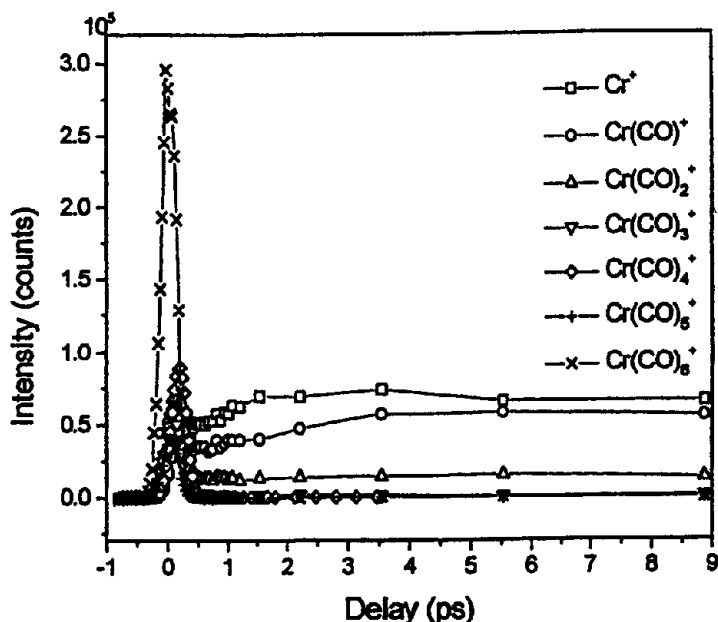


Figure 2. Ion yields for all species obtained with 267 nm (pump) and 800 nm (probe) pulses (parallel polarization).

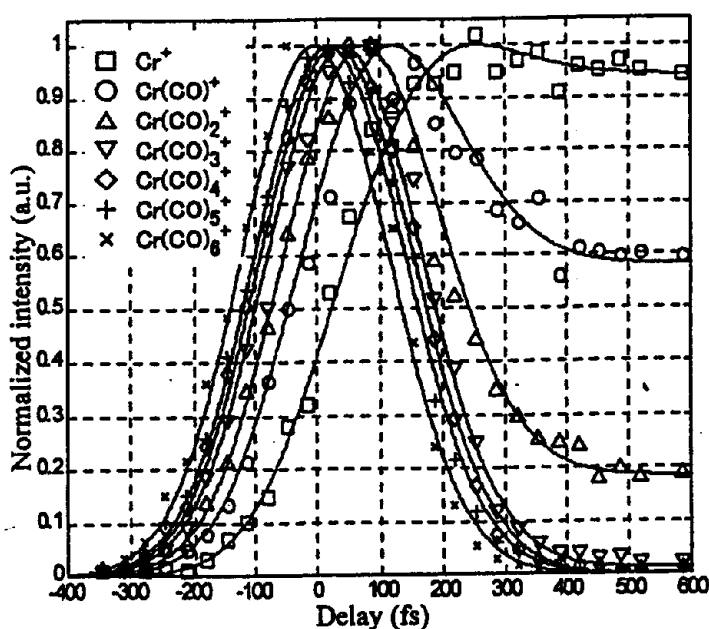
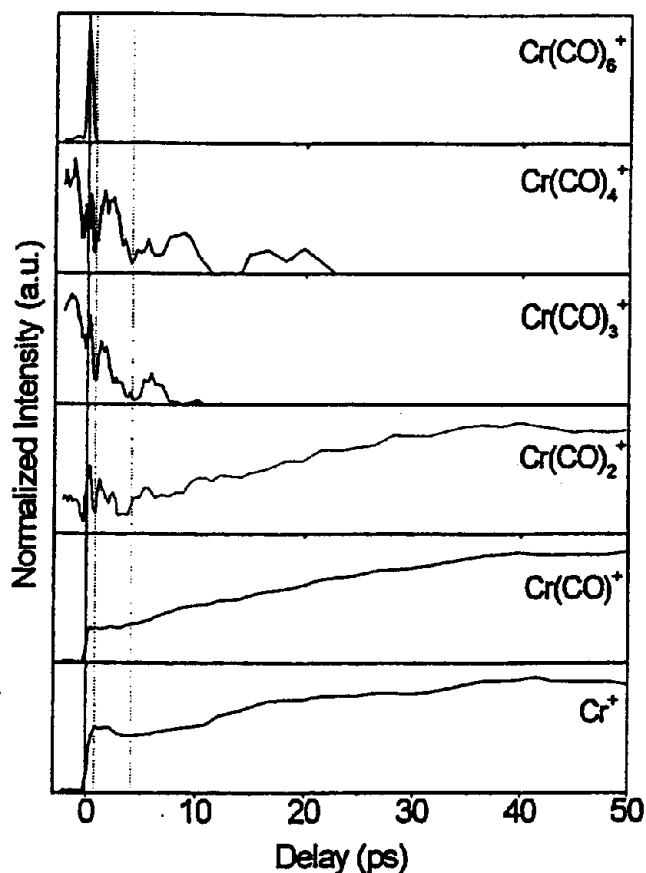


Figure 3. Normalized ion yields for 267 nm - 800 nm. Dots show experimental data and solid lines show simulation result.

20 fs respectively and the overall time that is needed for completing these fs sequential processes is 140 fs. The lifetime of the last state is in the time range of 10 ps or longer. When an individual lifetime was changed by times as small as 10 fs, significant error was introduced into the fit. Recently, Trushin, et al. reported similar results (8) for this system. Our results are in reasonable agreement with their study which incorporated a 5 level sequential process.

A constant signal from  $\text{Cr}(\text{CO})_n^+$  ( $n = 0\sim 3$ ) is observed between 1 and 10 ps. This signal is proposed to originate from the last long lived state of the sequential process. Since this constant signal is observed in  $\text{Cr}(\text{CO})_n^+$  with  $n = 0\sim 3$ , this long-lived state must belong to  $\text{Cr}(\text{CO})_n^+$ , where  $n = 3\sim 6$ . Moreover, the initial loss of CO ligand(s) from  $\text{Cr}(\text{CO})_6$  should occur during the 140 fs associated with the 7-state sequential process. This conclusion is further supported by our previous observation



**Figure 4.** Normalized ion yields for all species obtained with 200 nm (pump) and 400 nm (probe) pulses (parallel polarization).

us to access lower vibrational ionization states and avoid fragmentation by the probe pulse.

The peaks near zero time shift to longer times as the molecule sequentially loses CO ligands, as was also found for the 267 nm - 800 nm pump - probe experiment. This implies there is a similar type of mechanism that is operative. However, since the absolute intensity of these peaks for  $\text{Cr(CO)}_n^+$  ( $n = 2-4$ ) is extremely low, further experiments are needed to examine the near zero time trend more precisely.

A 2nd component is observed in the region of  $\sim 5$  ps with a life-time of approximately 2 ps. This time scale corresponds to rotational dephasing of the fragmented metal carbonyl complex. A 3rd component was also seen in the 5 - 50 ps region for  $\text{Cr(CO)}_n$  ( $n \leq 2$ ) showing a rise time of around 20 ps. This indicates there is a dissociation process with yet a longer time scale.

where it was found that the  $\text{Cr(CO)}_6^+$  ion is not observed when  $\text{Cr(CO)}_6$  is irradiated with a 2 ps pulse. The initial CO loss yields  $\text{Cr(CO)}_n$  where  $n = 3-5$  as the product species.

Normalized ion yields for all species obtained with 200 nm (pump) and 400 nm (probe) pulses (parallel polarization) are shown in Fig. 4. The data have been smoothed with 5-point averaging. The  $\text{Cr(CO)}_5^+$  signal is not displayed due to its extremely low signal level.

In the 200 nm - 400 nm pump - probe experiments, the peak at zero time is observed strongly for  $\text{Cr(CO)}_6^+$  but weakly for other fragment ions. This is presumably because the ground states of  $\text{Cr(CO)}_n^+$  ( $n = 2-5$ ) that are generated by the 400 nm probe have high vibrational energy and undergo rapid decomposition. To verify this hypothesis, we are planning a 200 nm - 800 nm pump - probe experiment which would enable

## CONCLUSIONS

We have completed experiments on the ultrafast ionization and dissociation dynamics of  $\text{Cr}(\text{CO})_6$  using femtosecond laser pulses. Multiphoton ionization of  $\text{Cr}(\text{CO})_6$  yields large molecular ion signals. Pump-probe experiments with 267 nm excitation reveal the presence of a fast sequential process in which rapid dissociation of Cr – CO bond(s) occur. The last product of this fs sequential process is considered to be one of  $\text{Cr}(\text{CO})_n$  ( $n = 3 \sim 5$ ). In the ultrafast experiments using 200 nm for the pump pulse, however, the intensity of the near zero time scale is extremely low or not observed for  $\text{Cr}(\text{CO})_n^+$  ( $n = 2 \sim 5$ ). This is presumably because the ground states of  $\text{Cr}(\text{CO})_n^+$  ( $n = 2 \sim 5$ ) generated by the 400 nm probe has high vibrational energy and undergoes rapid decomposition. The longer time scale component is also seen in  $\text{Cr}(\text{CO})_n$  ( $n \leq 2$ ) for up to 50 ps. This indicates the existence of a dissociation process with longer lifetime following the fs sequential mechanism. Further experiments using other probe wavelengths are planned.

## ACKNOWLEDGEMENTS

We are grateful for helpful discussions with Dr. Sergei Trushin. We also acknowledge the financial support of the National Institute of Health and the National Science Foundation.

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