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Time-Resolved Two-Laser Probe of $Cr(CO)_6$ Photodissociation Dynamics

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We have examined the photodissociation of jet-cooled $Cr(CO)_6$ using a time-resolved, two-laser multiphoton dissociation (MPD) technique with fluorescence detection of the atomic photofragments. We have observed that the rate of appearance of $Cr(CO)_4$ via 248-nm photolysis of $Cr(CO)_6$ is slower if the $Cr(CO)_6$ has first been cooled in a supersonic expansion. We suggest the difference in the observed rates is due to slower internal conversion in the transient $Cr(CO)_5$ following impulsive loss of the first CO ligand from the jet-cooled hexacarbonyl. This internal conversion is thought to be facilitated by low-energy OC–Cr–CO bending modes, which are probably not accessible by one-photon absorption from the ground state of $Cr(CO)_6$. We discuss the utility of our time-resolved MPD/atomic fluorescence technique as a general dynamical probe for metal carbonyl photodissociation.

Introduction

The photolability of organotransition metal compounds in general, as well as the volatility of many mono- and dinuclear homoleptic species, makes them interesting candidates for gas-phase photochemical studies.[1,2] It is well-established that gas-phase single-photon dissociation in such molecules leads to the cleavage of one or more metal–ligand bonds, depending on the energy of the photon,[2-6] and that absorption of several photons in the visible or UV region is accompanied by loss of all ligands.[7-10] Multiphoton dissociation (MPD) has been investigated as a means for the photochemical deposition of thin metal films,[11] has been utilized as a source of ground-state metal atoms for gas-phase kinetic studies,[12] and has been proposed as a source of neutral atomic precursors of selected states of metal ions for gas-phase reaction dynamics experiments.[13] An understanding of the detailed dynamics of the MPD of organotransition metal compounds would enable the optimization of photodissociation conditions in applications to problems of fundamental and applied significance.

Recently, the dynamics of MPD following pulsed laser irradiation of several organochromium[14,15] and organomolybdenum[16] species in gas cells has been examined. Observed state distributions of atomic metal photoproducts are accounted for in terms of a dynamical scheme encompassing two alternative photodissociation pathways. High-lying excited states of photoproduct atoms are thought to arise when a precursor molecule is optically pumped directly into the dissociative continuum and all of the metal–ligand bonds are broken in a concerted fashion. Low-lying states of photoproduct atoms are thought to arise from a sequential ligand loss mechanism involving at least one coordinatively unsaturated intermediate species. The electronic temperature describing the photoproduct atomic state distribution for the sequential mechanism is sensitive to the internal energy of the molecular intermediate. Whereas the observed emission spectrum from one-laser MPD provides a "snapshot" of this intermediate, the observed emission spectra from two-laser, time-resolved MPD provide a "motion picture" describing the dynamics of energy partitioning.

We report in this Letter our results from a study of the MPD dynamics of jet-cooled $Cr(CO)_6$ using a two-laser, time-resolved technique. Our results suggest that the electronic temperature describing the state distribution of atomic photoproducts in the sequential path is a function of *not only* the energy content of the coordinatively unsaturated intermediate but also the energy content of the saturated $Cr(CO)_6$ precursor.

Experiment

The experimental apparatus consists of a pulsed molecular beam valve fitted with a 0.5-mm nozzle, situated in one of the three orthogonal axes of a six-way cross. The two remaining orthogonal axes intersect the pulsed molecular beam 40 nozzle diameters downstream from the faceplate of the valve. Molecules in the beam are irradiated by pulses from two excimer pulses (222 nm, 5 mJ/cm^2; 248 nm, 30 mJ/cm^2) which enter from opposite ends of one arm of the cross. Synchronization of the molecular beam pulse and the two laser pulses is accomplished through the use of a multichannel delayed pulse generator. Emission from excited atomic photoproducts, as well as fluorescence resulting from laser excitation of atoms in nonemitting states, is collected along the axis orthogonal to both the molecular beam and the laser beams and dispersed by a monochromator.

Typically, 0.3 Torr of $Cr(CO)_6$ and 900 Torr of He are mixed in a gas manifold and expanded through the nozzle of the pulsed molecular beam valve. The first laser pulse at 222 nm creates two single-photon photoproducts, $Cr(CO)_4$ and $Cr(CO)_3$, in roughly equal amounts.[6c] In addition, a distribution of electronic states of Cr(I) arises due to multiphoton processes, either through direct MPD of $Cr(CO)_6$ or through secondary photodissociation of the coordinatively unsaturated primary photoproducts. These direct and sequential schemes are represented in reactions 1 and 2, respectively. Excited, emitting states of Cr(I), which are

$$Cr(CO)_6 + \geq 2h\nu \rightarrow [Cr(CO)_6]^* \rightarrow Cr + 6CO \quad (1)$$

$$Cr(CO)_6 + h\nu \rightarrow Cr(CO)_{x=3,4} + (2 \text{ or } 3)CO \quad (2a)$$

$$Cr(CO)_{x=3,4} + \geq 1h\nu \rightarrow Cr + (3 \text{ or } 4)CO \quad (2b)$$

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TABLE I: Radiative Lifetimes (ns) for Several Excited States of Cr(I)[a]

upper level	measured lifetime: this work	measured lifetime: previous work
$y^7P_4^0$	8	7
$t^5F_j^0$ (j = 1, 2)	35	
$v^5D_3^0$	6	
$z^7P_3^0$	33	33

[a] Emission lifetimes for this work are determined by deconvoluting from the fluorescence decay curve the Gaussian profile of the laser pulse and the exponential decay function of the photomultiplier tube. [b] Reference 17.

thought to arise primarily from nonsequential MPD as depicted in reaction 1, can be detected directly. Dark states of Cr(I) may be detected indirectly by laser-induced fluorescent excitation, provided that the laser pulse is of the correct wavelength. The coordinatively unsaturated primary photoproducts are invisible to the fluorescence detection scheme used by Tyndall and Jackson[14] and by Chaiken and co-workers.[15,16] In order to probe these photoproducts, thus providing information *complementary* to that obtained by one-laser photodissocation experiments, we employ a *second* laser pulse which can be delayed with respect to the first.

The second laser pulse at 248 nm is used to effect complete ligand stripping of the primary photoproducts, $Cr(CO)_{x=3,4}$, which result from the initial 222-nm photodissociation of $Cr(CO)_6$. Excited states of Cr(I) which can radiatively decay are detected directly, while the nonemitting a^5S and a^5D states are resonantly excited by the same 248-nm pulse and detected via laser-induced fluorescence. By using an appropriate delay between the two laser pulses, as well as spectral subtraction techniques which compensate for signal contributions due to one-color photodissociation processes, we can easily identify those features of the dispersed fluorescence spectrum which arises *exclusively* from MPD of the intermediate photoproducts, $Cr(CO)_{x=3,4}$. We observe experimentally that the intensities of the emission signals associated with the sequential ligand loss mechanism vary as the first power of the 222-nm laser fluence, while those features associated with concerted 222-nm MPD vary as the square of the 222-nm fluence. We are thus assured that the quintet features we observe are correlated with the appearance of a *molecular* photoproduct following one-photon dissociation of $Cr(CO)_6$ at 222 nm, rather than the direct production of quintet states of *atomic* chromium by 222-nm MPD.

Results and Discussion

Fluorescence Lifetime Measurements. A central assumption relating to the analysis of data from our two-color MPD experiment is that the temporal evolution of the various *atomic* photoproduct states, observed following the *second* laser pulse, reflects the evolution of primary *molecular* photoproducts following one-photon dissociation of the saturated precursor (in this case, $Cr(CO)_6$) by the *first* laser pulse. Several potential experimental artifacts may also influence the temporal evolution of these atomic states. For instance, at high number densities, collisional processes could lead to rapid relaxation of the nascent atomic state distribution. Collisional depopulation of high-lying atomic states, observed in emission, would cause the measured fluorescence lifetimes to be anomalously low. Collisional enhancement of low-lying state populations, upon which LIF transitions originate, would cause the measured fluorescence lifetimes for the corresponding emitting states to be anomalously high. In order to determine whether our observations are influenced by such artifacts, we measured the fluorescence lifetimes for several atomic states under a variety of experimental conditions and compared them with literature values.

The measured lifetimes of the z^7P^0, y^7P^0, t^5F^0, and v^5D^0 states of Cr(I) are listed in Table I. The septet states arise following concerted loss of all CO ligands from a molecular precursor which has been pumped directly into the dissociative continuum, while the two quintet states listed arise by 248-nm excitation of a^5S and a^5D states which are produced from $Cr(CO)_6$ in a sequential ligand loss mechanism. Measured lifetimes for the septet states are in agreement with available literature values.[17] The good agreement between our measured lifetimes and the literature values suggests that our experimental observations are not affected by either radiation trapping or collisional quenching. Tyndall and Jackson have measured fluorescence lifetimes for excited septet states of Cr(I) prepared by 248-nm MPD of $Cr(CO)_6$ which exceed literature values by more than an order of magnitude and have attributed these differences to radiation trapping.[14] Our experiment involves $Cr(CO)_6$ pressures which are 2–3 orders of magnitude less than those employed in the experiments of Tyndall and Jackson, so our observations are less likely to be perturbed by this artifact.

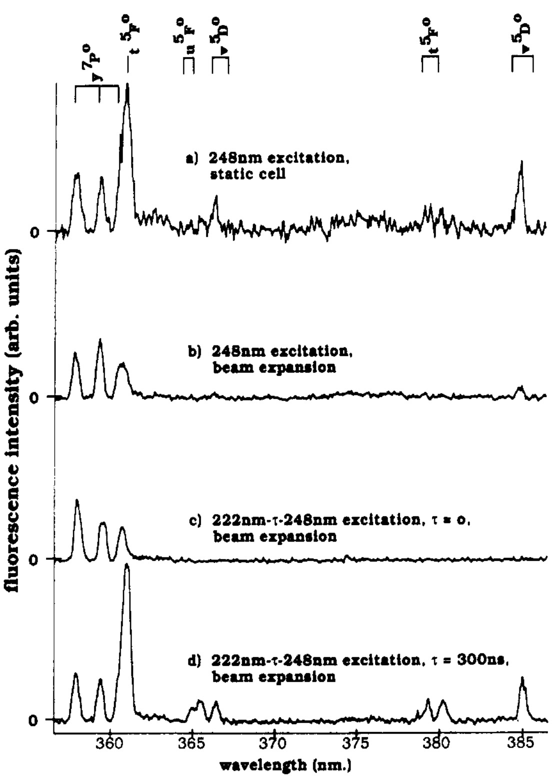

Figure 1. Dispersed fluorescence spectra collected following MPD of $Cr(CO)_6$. Term symbols for the Cr(I) upper levels for each of the observed transitions appear across the top of the figure. (a) 248-nm MPD of $Cr(CO)_6$ in a static cell at 300 K, $P_{\text{chamber}} = 5 \times 10^{-5}$ Torr. Spectra b–d utilized a He-seeded jet-cooled pulsed expansion operated at a repetition rate of 1 Hz, $P_{\max} = 3 \times 10^{-5}$ Torr. (b) 248-nm MPD of jet-cooled $Cr(CO)_6$. (c) Two-color MPD of jet-cooled $Cr(CO)_6$, zero delay. (d) Two-color MPD of jet-cooled $Cr(CO)_6$, 300-ns delay.

Dispersed Fluorescence Spectra following One- and Two-Color MPD. Four of the dispersed fluorescence spectra collected following MPD of $Cr(CO)_6$ are shown in Figure 1a–d. The spectrum in Figure 1a was generated by 248-nm MPD of $Cr(CO)_6$ which had been effusively introduced into the experimental chamber from a trap containing the solid hexacarbonyl at 300 K. Features in this spectrum can be assigned as emission from the y^7P^0, t^5F^0, u^5F^0, and v^5D^0 manifolds to lower-lying states of Cr(I). Note that the intense feature at 361.0 nm assigned as emission out of the t^5F^0 state overlaps with a weaker feature corresponding to one of the lines of the y^7P^0 multiplet. This spectrum is qualitatively similar to that obtained by Tyndall and Jackson. Features assigned to the septet system arise from radiative decay of excited Cr(I) atoms produced by *direct* MPD of $Cr(CO)_6$. Features assigned to the quintet system are LIF transitions pumped by 248-nm excitation of Cr(I) atoms in the low-lying dark states, a^5S and a^5D, which are produced by *sequential* MPD of $Cr(CO)_6$ through the intermediacy of an unsaturated photoproduct, presumably excited $Cr(CO)_4$.

The spectrum in Figure 1b was generated by 248-nm MPD of jet-cooled $Cr(CO)_6$ which was introduced into the experimental chamber in a seeded helium expansion. We note the conspicuous absence of emission lines belonging to the quintet system. Assuming that these quintet features are indicative of MPD via the sequential ligand loss mechanism, we are led to one of two alternative conclusions: either (a) one or more of the photoproducts in the sequential MPD of jet-cooled $Cr(CO)_6$ is collisionally quenched, or (b) sequential MPD of jet-cooled $Cr(CO)_6$ proceeds more slowly than for room-temperature $Cr(CO)_6$, such that less of the intermediate molecular photoproduct is produced *within the time interval of the laser pulse*. We discount the first alternative, since the results of simple hydrodynamic calculations[18] suggest that particles in the sampled portion of our molecular beam are not undergoing bimolecular collisions within the duration of the laser pulse. However, the idea that the primary (one-photon) 248-nm photoproduct arises more slowly from jet-cooled $Cr(CO)_6$ deserves further consideration.

On the basis of results from molecular beam photodissociation studies, Tyndall and Jackson[19] and Vernon and co-workers[20] both suggest that excited $Cr(CO)_4$ is the major product which eventually forms following 248-nm photodissociation of $Cr(CO)_6$. Furthermore, Vernon and co-workers suggest that the first CO ligand is lost in a highly nonstatistical fashion, leaving a nascent pentacarbonyl in its first electronic excited state. Statistical loss of the second CO requires that the nascent pentacarbonyl internally convert to its ground electronic state. This coupling, according to the SCF–CI calculations of Hay,[21] could be facilitated by in-plane bending of the metal–ligand bonds. Although this same photoproduct (i.e., vibrationally excited $Cr(CO)_4$ in its ground electronic state) should *eventually* form in our experiment, its rate of formation from jet-cooled $Cr(CO)_6$ is apparently lower than that from room-temperature $Cr(CO)_6$, low enough, in fact, that detectable levels of $Cr(CO)_4$ do not form in our one-color photolysis experiment within the time interval in which the laser pulse is on. We reason that a key step along the pathway to formation of $Cr(CO)_4$ is rapid internal conversion of the electronically excited pentacarbonyl to its ground electronic state, facilitated through distortion of OC–Cr–CO bond angle. From Vernon's thesis regarding the impulsive nature for loss of the first ligand from excited $Cr(CO)_6$, we infer that the exit channel is narrow and steep. If this exit channel is *sufficiently* steep, we would not expect excess energy to be partitioned into these OC–Cr–CO bending modes in the nascent pentacarbonyl. These modes will be populated in the pentacarbonyl *only* if the corresponding modes in the excited hexacarbonyl are already populated *prior* to ligand loss. Since these bending modes are not totally symmetric, dipole selection rules should formally forbid their excitation following one-photon absorption by ground-state $Cr(CO)_6$. In order to populate these modes in the nascent pentacarbonyl, it is thus necessary to have the correlated bending modes in the *ground-state* $Cr(CO)_6$ precursor already populated. One would expect that, for room-temperature $Cr(CO)_6$, a significant proportion of the total internal energy would be distributed among such low-energy vibrational modes. Jet-cooled $Cr(CO)_6$, having a tiny fraction of the total internal energy of its room-temperature counterpart, would have a negligible amount of internal energy in any given mode. Therefore, the nascent pentacarbonyl resulting from impulsive photoejection of CO from jet-cooled $Cr(CO)_6$ should undergo internal conversion at a slower rate than that produced from photolysis of room-temperature $Cr(CO)_6$, and statistical loss of the second CO would then occur later in the photodissociation of the jet-cooled precursor.

If our reasoning is correct, we expect that most, if not all, of the $Cr(CO)_4$ which is produced from one-photon dissociation of jet-cooled $Cr(CO)_6$ should appear at some time beyond the duration of the dissociating laser pulse. By employing a two-laser experiment where the second laser pulse is delayed with respect to the first, one should then be able to photodissociate thia $Cr(CO)_4$ to create the characteristic distribution of low-lying states of Cr(I) and subsequently observe the LIF transitions originating from the (nonemitting) a^5S and a^5D states, as seen in the room-temperature MPD experiments. In the two-laser experiment, jet-cooled $Cr(CO)_6$ is first irradiated with a pulse of 222-nm light.[22] After a given temporal delay, the 222-nm photoproducts are then irradiated by the 248-nm laser pulse, and any pure emission from high-lying Cr(I) states, as well as any LIF emission pumped from low-lying states, is collected and dispersed. The spectrum in Figure 1c was acquired using a delay of zero between the initial 222-nm pulse and the subsequent 248-nm pulse, while that in Figure 1d was acquired using a delay of 300 ns. While the former two-laser spectrum resembles the one-laser fluorescence spectrum of Figure 1b, the latter displays the quintet features diagnostic of the sequential pathway for MPD of $Cr(CO)_6$. We monitored the intensity of the quintet emission features over a wide range of delay times between the 222- and 248-nm laser pulses. As the delay increases from zero to several tens of nanoseconds, the quintet signal grows in and then levels off to an intensity near that of Figure 1d for delays greater than 200 ns. At delay times exceeding a few microseconds, we are unable to observe *any* fluorescence. We were able to model this signal attenuation simply by accounting for diffusion of photoproducts out of the collection volume of the monochromator at the nominal velocity of the molecular beam.

The experimental observation of nonstatistical energy release in the single-photon dissociation of transition-metal coordination compounds is not without precedent. Vernon and co-workers were able to fit metal carbonyl photoproduct translational energy distributions, following UV dissociation of jet-cooled group VIB hexacarbonyls, to a *hybrid* model where loss of the first CO is impulsive and sequential loss of additional CO ligands is statistical. The rigorously statistical model was incapable of satisfying both the product branching ratios (observed in other experiments) and the translational energy distributions.[20] Grant and co-workers used a 2 + 2 REMPI scheme to measure the CO photoproduct vibrational state distribution following near-UV photolysis of $Fe(CO)_5$ and found that the CO product is formed in an inverted vibrational distribution.[23] This interpretation conflicts with the results of Waller and Hepburn, who used vacuum-ultraviolet LIF to probe the rovibrational state distribution of CO photoproduct from UV photolysis of jet-cooled $Fe(CO)_5$.[24] In these experiments, populations of the three lowest vibrational levels of CO were adequately predicted by a simple statistical model, although measured populations of low-lying ($J < 10$) rotational states for CO(v=0) were consistently greater than predicted by this model. Holland and Rosenfeld used transient diode laser absorption spectroscopy to probe rovibrational and translational energy release to the CO product following 351-nm photolysis of $W(CO)_6$.[25] They found that energy disposal could be adequately predicted only by a *modified* phase space theoretical treatment, in which vibrational energy release occurs earlier in the exit channel than rotational or vibrational release. Buntin et al. used vacuum-UV–LIF to probe energy release to the CO product following both 266- and 355-nm photolysis of jet-cooled $Mo(CO)_6$.[26] While the rotational state populations for $v = 0$ and $v = 1$ could be fit to Boltzmann distributions, it was not possible to predict both the vibrational and rotational temperatures from phase space theory, early phase space theory, or the separate statistical ensembles model. Clearly, while limiting-case statistical treatments often enable us to predict many of the features of organometallic photodissociation, they fall short of providing a complete picture of photodissociation dynamics. Although the topology of the relevant potential energy surfaces for metal carbonyl photodissociation has yet to be elucidated, we believe the results of the current experiments represent an example of the effects of potential surface shape on energy release dynamics.

We now consider an alternative explanation for the rate behavior observed in the present experiments. We have proposed that the rate-limiting step in the overall two-photon dissociation of $Cr(CO)_6$ is the internal conversion of the nascent, electronically excited pentacarbonyl to the ground electronic surface. A possibility which we are unable to rule out is that $Cr(CO)_3$, rather than $Cr(CO)_4$, is the key one-photon intermediate which subsequently undergoes multiphoton dissociation to give the low-lying quintet states of chromium observed via LIF. Weitz and co-workers have suggested that $Cr(CO)_3$ is also a minor product in the 248-nm dissociation of $Cr(CO)_6$.[5] $Cr(CO)_3$ should form relatively slowly from the high-energy tail of the nascent photoproduct population following initial photon absorption, and its formation may in fact be rate limiting in the overall two-photon process. One could prevent the formation of Cr(CO)$_3$ by eliminating this high-energy tail, for example, by collisionally quenching the unsaturated intermediate, as in the experiments of Tyndall and Jackson.[14]

To summarize, the photoproducts we are probing in this two-laser experiment appear to arise from one-photon dissociation of Cr(CO)$_6$ and are therefore molecular, rather than atomic. Although the LIF signals we observe in the two-color spectrum in Figure 1d are interpreted in terms of a Cr(CO)$_4$ intermediate, we cannot be sure to what extent photodissociation of the Cr(CO)$_3$ photoproduct is also contributing to the observed LIF signal intensity. These preliminary results indicate the general utility of a two-laser, time-resolved approach incorporating state-specific atomic detection as a dynamical probe of metal carbonyl photodissociation.

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Mode Specific Photodissociation of the $^1B_2$ State of CS_2

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We report results on the dynamics and spectroscopy of the predissociating $^1B_2$ state of CS$_2$, excited at wavelengths around 200 nm. The atomic S product electronic state branching ratio is a strong function of which band in the $^1B_2(^1\Sigma^+_u) \leftarrow X^1\Sigma^+_g$ system is pumped. $K = 0$ bands lead to mostly S($^3P_2$) products, while $K = 1$ bands produce much less S($^3P_2$) and show a marked enhancement of S($^1D_2$).

One of the longstanding motivations behind the detailed study of small molecule photodissociation dynamics has been the search for mode specificity in photochemistry. Although there have been many different approaches taken to this goal, the common definition of mode specificity is the ability to favor through selective excitation one specific product channel from a number of allowed channels. Some recent examples of this illustrating different approaches are the work of Lee and co-workers on CH$_2$IBr[1] and the work of Crim and co-workers on H$_2$O[2]. In the first case, pumping a band corresponding to a dissociative state localized on the C–Br bond led to preferential scission of that bond. The second experiment used vibrational overtones of either the O–H or O–D local mode to select the dissociating bond. In both cases, the initial excitation was made in a way that "localized" the energy in a particular bond in the molecule, followed by preferential scission of that bond.

In this paper we report observation of a different form of selective photochemistry, in which the electronic states of the product are selected through selective excitation. The present results are in some sense related to previous work on spin–orbit fine structure distributions resulting from photofragmentation.[3] As an example, in recent work Butler and co-workers observed an increased yield of I($^2P_{3/2}$) product from CF$_3$I photolysis resulting from heating the parent molecule.[4] The authors attribute this change to increased population of bending vibration excited states in the CF$_3$I molecule, resulting in an enhanced coupling to the dissociating surface correlating to the I($^2P_{3/2}$) product. The results reported here concern not only fine structure states in an

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