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**MULTIPHOTON IONIZATION OF
GROUP VI B HEXACARBONYL VAN DER WAALS CLUSTERS:
TRENDS IN INTRACLUSTER PHOTOCHEMISTRY**

by

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Multiphoton Ionization of Group VIB Hexacarbonyl van
der Waals Clusters: Trends in Intracuster
Photochemistry

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Abstract

Van der Waals clusters of $M(CO)_6$ ($M=Cr, Mo, W$) generated in the free-jet expansion of a pulsed beam of seeded helium are subjected to multiphoton ionization (MPI) and the product ions analyzed by quadrupole mass spectrometry. We previously reported the observation of efficient production of MoO^+ and MoO_2^+ following MPI of $Mo(CO)_6$ van der Waals clusters, and proposed that these ions arise through novel reactions between a neutral photoproducted metal atom and the ligands of an adjacent metal carbonyl "solvent" molecule within the cluster. In order to test some of the predictions of this model, we have now examined the MPI of van der Waals clusters of the other Group VIB hexacarbonyls. We find the same novel behavior (viz., efficient production of metal oxide ions) in the $W(CO)_6$ system as that previously observed for $Mo(CO)_6$. However, we find no evidence of such behavior in the $Cr(CO)_6$ system. Based on these observations, we suggest that the reactivity of first-row transition metal atoms may be fundamentally different from that of second- or third-row metals. These differences are discussed in terms of the occupancy and relative size of the metal d orbitals.



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Introduction

Transition metal carbonyl complexes have been the subject of intense research by both theorists¹ and experimentalists.^{2,3} The variety exhibited in the types of bonding between metals and carbonyl ligands challenges our chemical intuition.⁴ Many coordinatively unsaturated metal carbonyl species are thought to play important roles in catalytic cycles.⁵ Such unsaturated species can be efficiently generated in the gas phase via pulsed laser photolysis of the corresponding saturated species; in fact, these unimolecular photofragmentation reactions provide a convenient means for testing and refining statistical reaction rate theories.⁶

Time-resolved infrared spectroscopy (TRIS) has been used to study the dynamics of excimer laser photolysis of transition metal carbonyls, the details of energy partitioning along the reaction coordinate, and the recombination kinetics of primary photoproducts with various ligands.^{7,8} The temporal dependence of certain features in the infrared spectra suggest that coordinatively unsaturated metal carbonyl species undergo clustering reactions with their saturated precursors at approximately gas kinetic rates.⁹⁻¹⁰ For example, the clustering reaction



proceeds in the gas phase with a rate constant of $1.8 \times 10^7 \text{ Torr}^{-1} \text{ sec}^{-1}$ at 300 K.⁹ Group theoretical analysis¹⁰ of IR spectroscopic data (i.e., the number and relative intensities of observed absorption bands) is especially useful in assigning structures to the mononuclear carbonyl fragments. However, the products of clustering reactions such as the one above are less amenable to such an analysis because of the lower symmetry of these binuclear species and overlap with the spectral features of other species. It is necessary to study these metal carbonyl clustering reactions by some complementary tech-

nique if one hopes to derive detailed information on structure and bonding. One technique which holds promise as a structural probe of these clustering reactions is multiphoton ionization mass spectroscopy (MPI/MS). The multiphoton dissociation and ionization dynamics of mononuclear²⁰⁻²² and covalently bound multinuclear²³⁻²⁶ transition metal carbonyls is well understood: initial multiphoton dissociation (MPD) of the metal carbonyl results in complete ligand stripping, leaving behind a naked metal atom which is subsequently ionized. Consequently, the MPI mass spectrum is dominated almost exclusively by the metal ion signal. On the other hand, the multiphoton photophysics of van der Waals complexes of transition metal carbonyls is not so thoroughly characterized. Such van der Waals complexes are inherently interesting, since multiphoton processes within these complexes may lead to the production of coordinatively unsaturated transient species clustered within a shell of saturated "solvent" molecules. These photoproducts could serve as model systems in the study of phenomena such as heterogeneous catalysis or chemisorption on metal surfaces. Clustering reactions (such as those inferred from TRIS experiments) within these complexes should be easily stimulated, and would perhaps give rise to anomalous fragment ion yields in the mass spectrum. Indeed, novel intracluster chemistry has been observed to accompany the multiphoton dissociation of mixed van der Waals complexes composed of $\text{Fe}(\text{CO})_5$ and small oxygen-containing molecules.²⁷

In order to explore the interplay between unimolecular photodissociation processes and bimolecular reactivity in metal carbonyls, we have examined the MPI/MS of van der Waals complexes of Group VI hexacarbonyls. We recently reported the observation of novel behavior in the multiphoton dissociation and ionization of $\text{Mo}(\text{CO})_6$ van der Waals complexes.²⁸ Efficient production of MoO^+ and MoO_2^+ ions following multiphoton excitation of the metal carbonyl van der

Waals complexes led us to propose the intermediacy of a structure (or structures) containing doubly-bridging carbonyls acting as four-electron ligands, as illustrated in Figure 1, where M^* is a nascent metal atom which interacts strongly via $d-\pi^*$ back-bonding with the oxygen ends of adjacent carbonyl ligands within the neutral van der Waals complex. One of the predictions of this model is that for smaller metal atoms, the metal d orbitals will be more contracted and the bridging carbonyls will thus be forced into closer proximity. Crowding of the bonding π orbitals of the bridging carbonyl ligands (within the $CO-M^*-CO$ plane) will tend to be destabilizing, and if this repulsive interaction is not overcome by the strength of the M^*-O bonds, this type of doubly-bridged structure will not form. Consequently, yields for MO^+ and MO_2^+ should be diminishingly small, if not totally absent, when M is a metal whose d shell is of small diameter. In order to test this structural model, we have examined the MPI/MS of van der Waals complexes of metal carbonyls other than that of molybdenum. We describe herein our results for $Cr(CO)_6$ and $W(CO)_6$ complexes, and discuss implications for intracluster reactivity and bonding.

Experimental Section

The metal carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, were obtained from Aldrich in purities of 99%, 98%, and 99%, respectively. Prior to use, each compound was further purified by several freeze-pump-thaw cycles at 77 K. Our cluster beam photoionization mass spectrometer is shown in Figure 2 and has been described elsewhere in detail.²⁸ Briefly, helium seeded with a metal carbonyl compound at its room temperature vapor pressure (typically a few hundred mTorr) is admitted into the low-volume stagnation region of a Newport BV-100 pulsed molecular beam valve fitted with an end plate having a 0.5 mm diameter, 30° conical aperture. The stagnation pressure of the seeded helium is

1.3 atm. Metal carbonyl van der Waals complexes are formed in the free-jet expansion of the pulsed beam of seeded helium. The background pressure inside the vacuum chamber with the pulsed beam valve off can be maintained at less than 10^{-7} Torr, and operation of the valve at 1 Hz leads to maximum chamber pressures of about 3×10^{-6} Torr. The cluster beam pulse is directed axially into the ion source of a Dycor M200M quadrupole mass spectrometer, where it is intersected by the focused output from a Lambda Physik EMG 150 excimer laser, operated on the KrF* transition at a pulse energy of ca. 100 mJ. Synchronization of the laser and the molecular beam valve is accomplished through the use of an external timing circuit with an adjustable delay. The timing circuit is set to fire the 20 nsec laser pulse on the leading edge of the ca. 150 μ sec duration molecular beam pulse. Ions produced in the ion source are selected by the quadrupole mass filter and detected by a low gain (ca. 1000X) electron multiplier. Output from the multiplier is converted to a voltage, amplified by a fast 100X amplifier, and averaged with background subtraction by a boxcar averager (EG&G Princeton Applied Research, Model 4420). Typically, the mass filter is scanned at a rate of 0.04 amu/sec over a 100-amu range so that spectra may be collected and averaged for 2500 laser shots.

Electron impact (EI) mass spectra of the van der Waals complexes can also be collected by leaving the excimer laser off and energizing a thoriated iridium filament within the ion source. Typically, we operated this source at an electron energy of 70 eV and an emission current of 1 mA. In addition, mass spectra of the unclustered metal carbonyls (i.e., "monomers") may be collected by admitting the neat sample vapor directly through an effusive inlet. In order to properly interpret data from cluster beam ionization experiments, one must verify that the observed ion signals result from ionization of neutral species within the molecular beam, rather than ionization of residual

molecules within the vacuum chamber. Since we are able to adjust the delay time between the triggering of the pulsed beam valve and the firing of the laser, we can determine the temporal behavior of the ion signal and thereby ensure that the ions we are creating actually arise from neutrals in the molecular beam.

Results and Discussion

Relevant portions of the MFI mass spectra of the van der Waals complexes of Mo(CO)_6 , W(CO)_6 , and Cr(CO)_6 are shown in Figures 3, 4, and 5, respectively. The MFI mass spectra of the corresponding unclustered metal carbonyls are shown alongside for comparison. We have previously discussed our results for the Mo(CO)_6 system.²⁸ We observed the efficient production of MoO^+ and MoO_2^+ ions following multiphoton ionization of van der Waals complexes of the hexacarbonyl. We noted that such ions are not observed in the MFI mass spectrum of the unclustered, monomeric hexacarbonyl,²⁰ nor are they observed in electron impact (EI) mass spectra of either monomers or clusters. From the temporal behavior of these oxo- and dioxomolybdenum ions, we reasoned that these ions were originating from novel intracluster photochemical reactions, reactions which most likely take place between two neutral participants within the van der Waals complex. Based upon orbital symmetry arguments and analogies from surface science²⁹ and synthetic organometallic chemistry,^{30,31} we proposed the intermediacy of a structure such as 1 (vide supra) to account for the observed photochemistry. Similar types of structures have been proposed to account for observed trends in ion-molecule reactivity among coordinatively unsaturated transition metal carbonyls.³²

As discussed above, one of the implications of our structural model is that bridging by two carbonyl ligands will be stable only if the d_{xy} orbital

on M^* is sufficiently large to prevent crowding of the occupied π orbitals of the bridging carbonyls. We would expect, based on our results with Mo, that an atom such as W might be able to interact with the oxygen ends of the two bridging carbonyls via back-donation from its valence $5d_{xy}$ orbital. We therefore expect van der Waals complexes of $W(CO)_6$ to exhibit the same type of novel photochemical behavior following multiphoton excitation as that observed previously in the $Mo(CO)_6$ system. In fact, we do observe efficient production of WO^+ , as shown in Figure 4. We emphasize that WO^+ is *only* observed in the MPI mass spectrum of $W(CO)_6$ van der Waals complexes. It is *not* observed in the MPI mass spectrum of the unclustered hexacarbonyl, nor is it observed in any of the EI mass spectra. We believe that production of WO^+ is occurring through the same type of novel intracluster photochemical mechanism as that previously proposed for the $Mo(CO)_6$ system; that is, reaction between a photo-produced W atom and the oxygen ends of carbonyl ligands on an adjacent $W(CO)_6$ "solvent" molecule within the van der Waals complex. Our mass spectrometer is only able to pass ions of $m/z \leq 210$, and we are therefore unable to detect WO_2^+ product ions (m/z 214, 215, 216, and 218).

We now consider the remaining member of the homologous series, $Cr(CO)_6$. Figure 5 shows a portion of the MPI mass spectrum of $Cr(CO)_6$ van der Waals complexes. One immediately notices that the photophysical behavior of the $Cr(CO)_6$ system differs from that of the other Group VIB hexacarbonyls. No metal oxide ions are observed in the mass spectrum; instead, van der Waals complexes appear to behave just like the unclustered monomer, yielding a mass spectrum dominated by the metal ion signal. Operation of the pulsed molecular beam valve at ca. three-fold higher intensity (maximum chamber pressure of about 10^{-5} Torr) results in the production of a series of ions, $CrOH_x^+$ ($x=0,1,2$), which presumably form upon MPD/MPI of heteroclusters of $Cr(CO)_6$ and

H₂O (present as an impurity in the helium gas cylinder). These ions are also seen in the high-pressure EI spectrum. However, MPI spectra recorded under conditions of lower pulsed molecular beam intensity show no ion signals corresponding to CrO⁺ or CrO₂⁺. One might suspect that we are simply not creating Cr(CO)₆ van der Waals complexes in our seeded expansion when the pulsed valve is operated at lower intensity. However, we feel confident for the following reasons that cluster formation is indeed taking place. First, we know that Cr(CO)₆ vapors are mixing into the helium buffer gas and diffusing toward the nozzle, because we observe crystalline deposits of Cr(CO)₆ inside the stagnation volume of the pulsed valve after several hours of operation. Second, we have demonstrated (in other, unrelated cluster EI/MS experiments in our lab) that the nozzle geometry we employ allows for facile generation of a large distribution of cluster sizes from seeded rare gas expansions. Third, we have previously shown that clustering *must* be taking place in the expansion of Mo(CO)₆ seeded in helium, based on the temporal behavior of the metal oxide photoions. Since the vapor pressures of Mo(CO)₆ and Cr(CO)₆ are comparable, and since the conditions of stagnation pressure and pulsed beam intensity and duration for the Cr(CO)₆ expansion are identical to those used previously for the Mo(CO)₆ expansion, we would likewise expect clustering to take place in a seeded Cr(CO)₆ expansion. Finally, since we are apparently able to generate heteroclusters of H₂O and Cr(CO)₆, even though the number density of H₂O molecules in the seeded gas is estimated to be an order of magnitude less than that of the metal carbonyl, we should have no difficulty generating clusters of Cr(CO)₆.

Why is it that Cr(CO)₆ van der Waals complexes should display photophysical behavior unique among Group VIB hexacarbonyls? One possibility is that intracluster bimolecular reactions simply are not taking place within the

Cr(CO)₆ van der Waals complexes, although this is inconsistent with the results of kinetic studies which infer that gas-phase clustering reactions between Cr(CO)₆ and its coordinatively unsaturated photoproducts take place at gas-kinetic rates.⁹⁻¹¹ Two more likely possibilities merit consideration: one, that clustering reactions between the nascent Cr atom and adjacent Cr(CO)₆ "solvent" molecules occur via the same symmetrically bridged intermediate proposed for the Mo(CO)₆ and W(CO)₆ systems, but involve much weaker and, consequently, more photolabile M*-O interactions; or alternatively, that clustering reactions in the Cr(CO)₆ system are mediated through a different bonding scheme, perhaps one involving unsymmetrical bridging and/or significant metal-metal bonding interactions. We discuss these two alternatives below.

Let us first examine the possibility that the nascent Cr atom reacts with an adjacent hexacarbonyl molecule within the van der Waals complex to form a structure analogous to the one proposed earlier for the Mo(CO)₆ and W(CO)₆ systems. As an approximation, we will impose the constraint that the two symmetrically bridging carbonyls (whose interatomic axes we shall take to be roughly parallel) are separated by the van der Waals "thickness" of a π orbital, approximately 3.4 Å.³³ For a planar structure with C-O-M* bond angles of 120°, each of the two M*-O bonds would have a length of about 2 Å. If the separation of the bridging carbonyls is maintained and the O-M*-O bond angle is decreased from 120° to 100° (a value typical of some metal acetylacetonates³⁴), the M*-O bond length increases to about 2.2 Å. For which (if any) of the Group VIB metals is this range of M*-O bond lengths reasonable? Estimated M*-O bond lengths based on atomic nonpolar covalent radii³⁵ are 1.91 Å (M*=Cr), 2.03 Å (M*=Mo), and 2.03 Å (M*=W). Experimental bond lengths for a variety of dioxygen-metal complexes have been tabulated:³⁶ typical metal-

oxygen bond lengths for complexes of Cr range from 1.81 to 1.92 Å; and for those of Mo, from 1.91 to 2.24 Å.³⁷ Based on our estimated metal-oxygen bond lengths and available experimental data, we believe that ground-state atoms of Mo or W might reasonably be expected to undergo clustering reactions with the corresponding metal hexacarbonyls to form structures such as 1, while ground-state Cr atoms would be more likely to form some alternative structure as a result of clustering reactions with Cr(CO)_6 .

One such alternative might be a structure in which the Cr atom interacts via unsymmetrical bridging with one (or more) of the CO ligands of the neighboring hexacarbonyl, as suggested in Figure 6. In this bonding scheme, the CO ligand is terminally bound to one metal center, but side bound to the other. This type of bonding has been invoked to explain the relatively low gas-phase reactivity of $\text{Mn}_2(\text{CO})_{10}$ toward recombination with CO.³⁸ We cannot discount the possibility that the two Cr atoms might be bridged exclusively through the carbon end of a bridging carbonyl, in a monohapto- fashion, although such bonding would involve a fairly substantial geometric rearrangement of the Cr(CO)_6 reactant.

It is interesting to speculate on how the bimolecular reactivity of Cr would change in the present case if it were to possess occupied 4d orbitals which could participate in bonding interactions with the ligands of an adjacent Cr(CO)_6 molecule. This would require that the nascent Cr photoproduct be produced in an excited state. The lowest excited state with non-zero occupation of the 4d orbitals is the $e\ ^7D$ state; its $J=1$ component is 42253.42 cm^{-1} (ca. 5.24 eV) above the Cr $a\ ^7S$ ground state.³⁹ It is known from emission studies that MPD of Cr(CO)_6 at 248 nm produces atomic Cr in a statistical distribution of states;⁴⁰ thus, one would expect the ground state of Cr to be the predominant species produced in our experiment. While the excited $e\ ^7D$ state

is not one-photon accessible from the a^7S ground state, it certainly is accessible via a two-photon transition; one would therefore expect production of a significant population of e^7D Cr atoms upon MPD of $Cr(CO)_6$ using focused laser pulses at about 473.3 nm. These excited Cr atoms, by virtue of their 4d orbital electron density, might display the same kind of bonding interactions with metal carbonyls as we have inferred above for ground-state Mo and W atoms.

Conclusions

We have examined the 248 nm multiphoton dissociation and ionization dynamics of van der Waals clusters of the Group VIB hexacarbonyls. Mass spectral evidence indicates that W atoms undergo the same novel photoinduced bimolecular intracluster reactions previously inferred for Mo, while Cr atoms do not. We suggest that this trend in reactivity is due primarily to changes in the spatial extent of the valence d orbitals. Furthermore, such an interpretation may imply enhanced reactivity of higher excited states of third-row transition metals produced within the cluster environment. We are currently extending our studies to other third-row transition metal carbonyls in order to refine our understanding of the photochemistry of van der Waals clusters.

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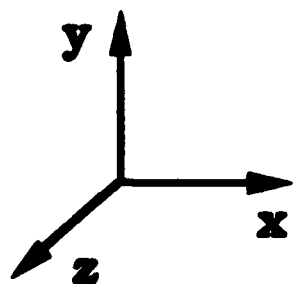
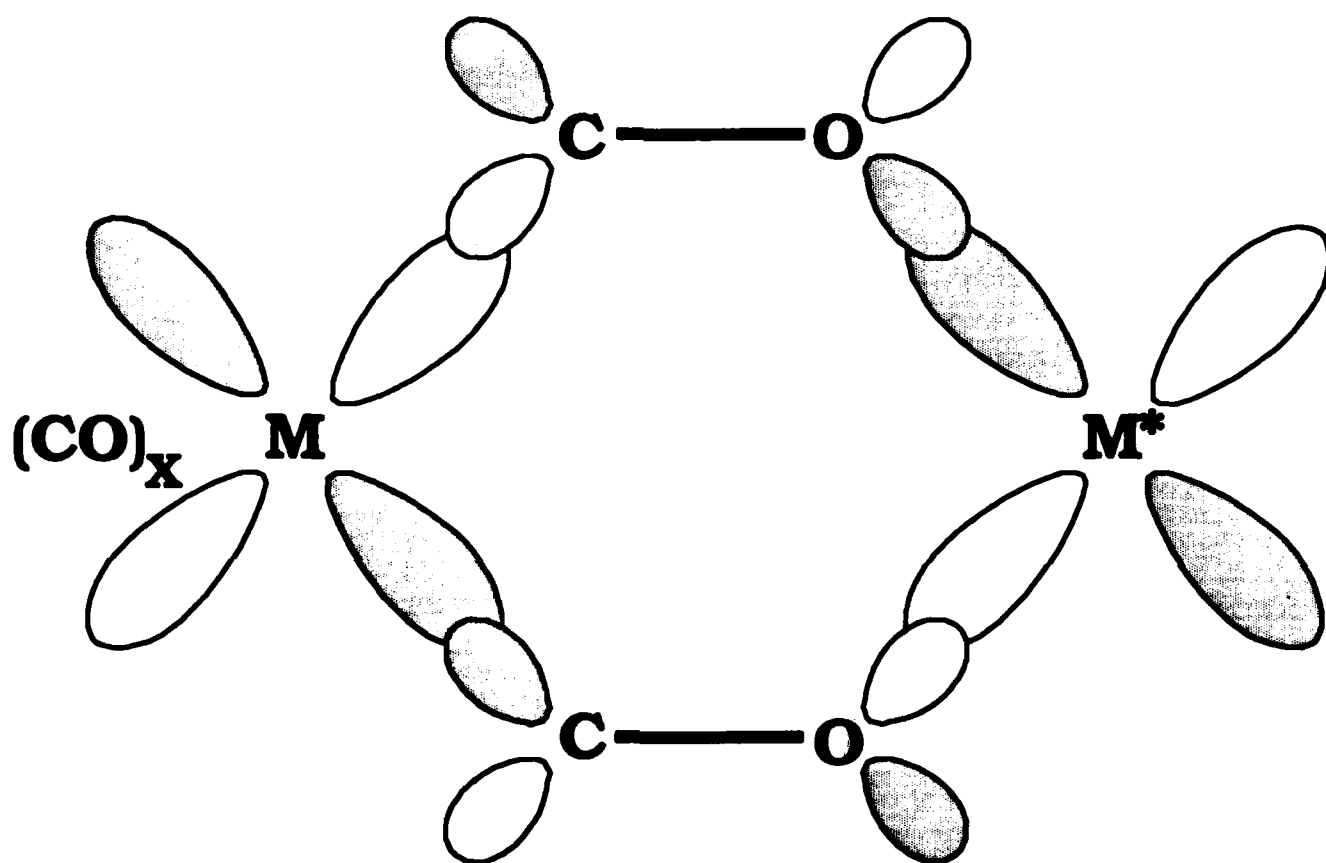
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Figure 1. Proposed structure for the product of a clustering reaction between a photoproducted metal atom, M^* , and a neighboring metal carbonyl "solvent" molecule within a van der Waals cluster (see reference 28). The value of x may range from 0 to 4. Back-donation from the occupied metal d_{xy} orbitals to the carbonyl π_y^* anti-bonding orbitals is illustrated.



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Figure 2. Cluster beam photoionization/mass spectrometry experiment, shown schematically.

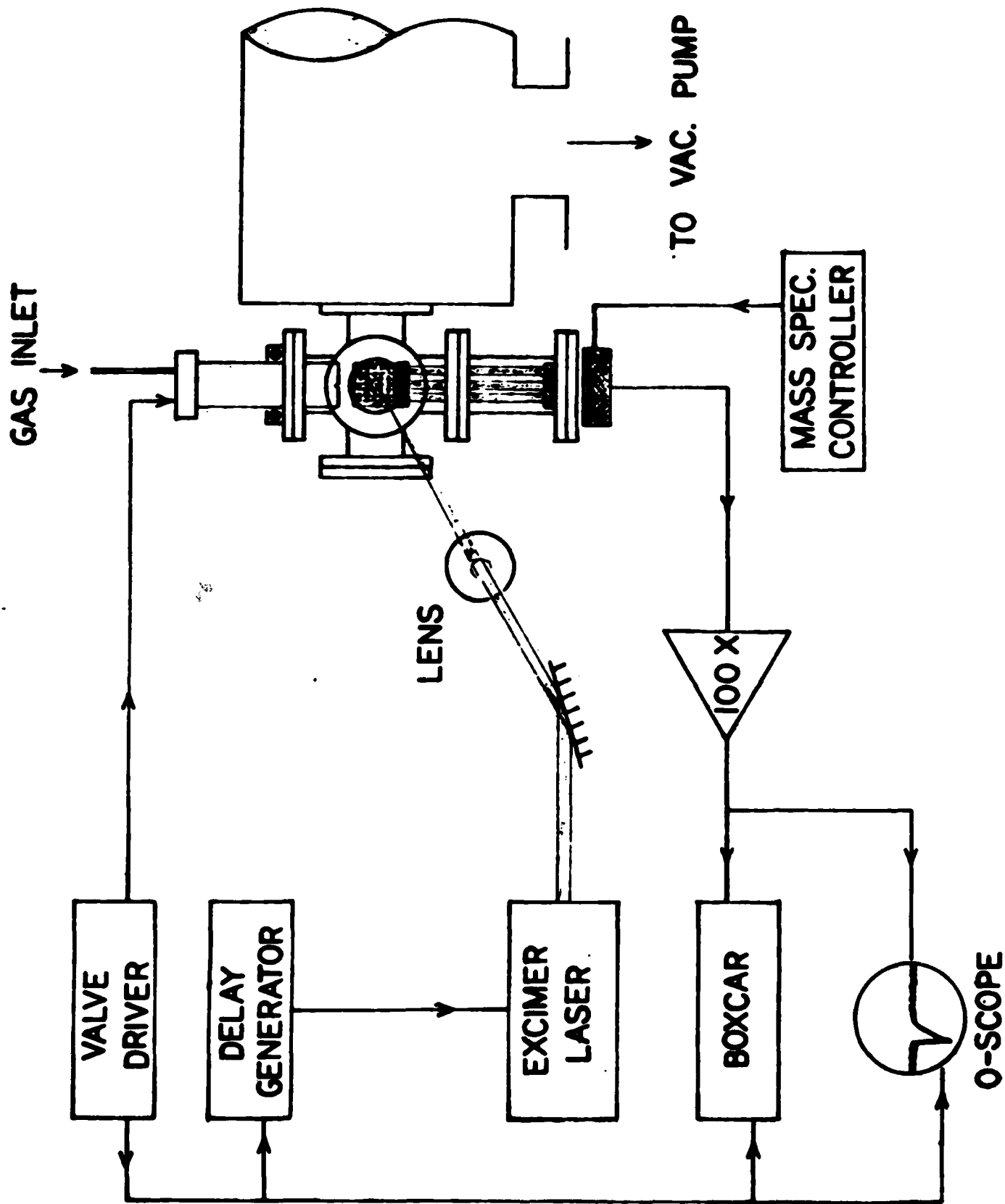


Figure 3. (A) MPI mass spectrum of Mo(CO)_6 van der Waals clusters, 80-160 amu. Signal due to ions of $m/z \geq 101$ amu is amplified by a factor of 10. (B) MPI mass spectrum of the unclustered Mo(CO)_6 , 80-160 amu, shown for comparison. As above, ion signal is amplified by a factor of 10 for ions of $m/z \geq 101$. Note the absence of oxo- and dioxomolybdenum ions in the mass spectrum of the unclustered Mo(CO)_6 .

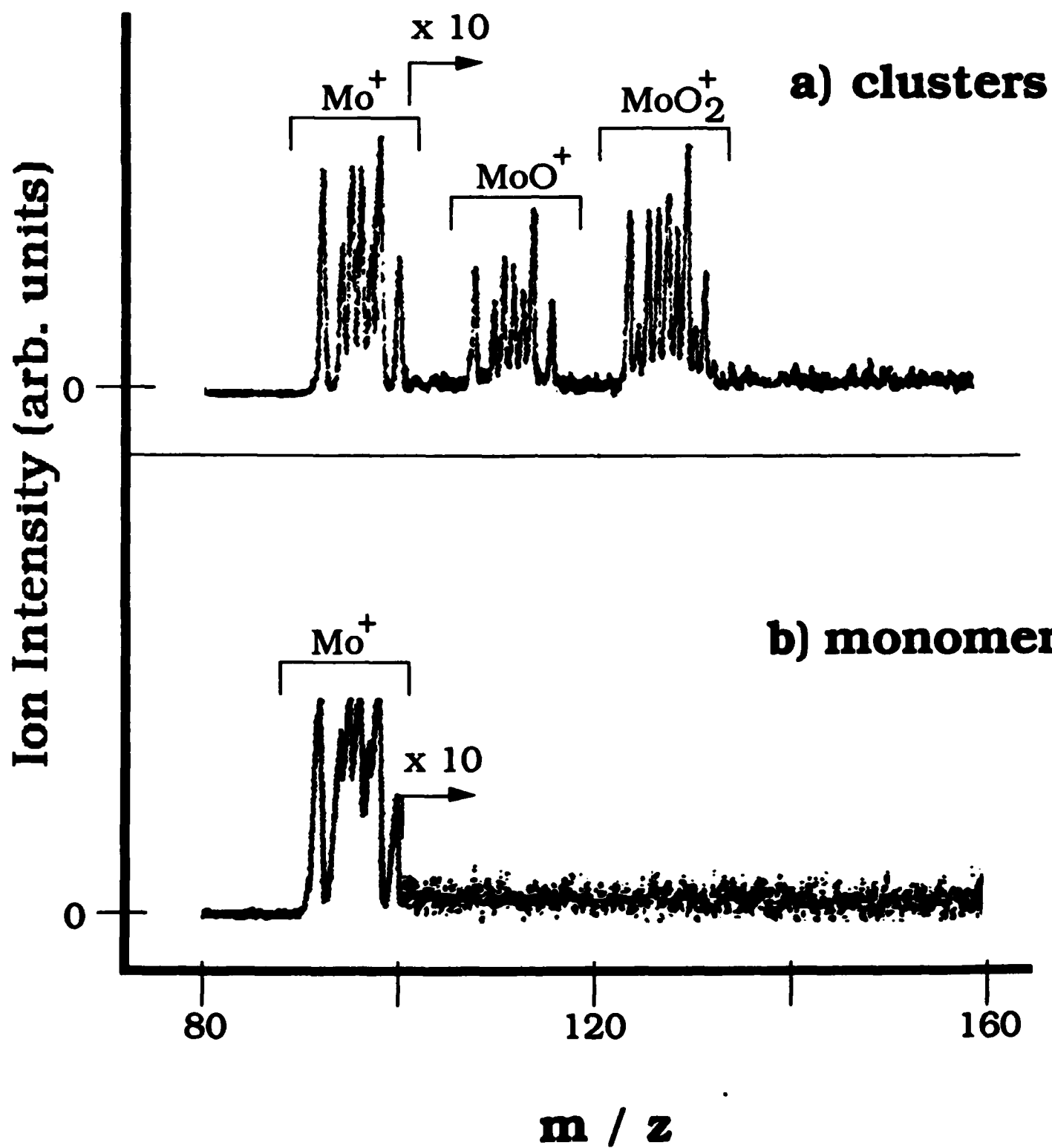


Figure 4. (A) MFI mass spectrum of $W(CO)_6$ van der Waals clusters, 170-210 amu. Signal due to ions of $m/z \geq 190$ amu is amplified by a factor of 25. WO^+ ions are clearly visible, although limitations of our quadrupole mass filter prevent us from detecting any WO_2^+ ions which might be produced. See discussion in text. (B) MFI mass spectrum of the unclustered $Mo(CO)_6$, shown for comparison. As above, ion signal is amplified by a factor of 25 for ions of $m/z > 190$. Note the absence of WO^+ ions in the mass spectrum of the unclustered $W(CO)_6$.

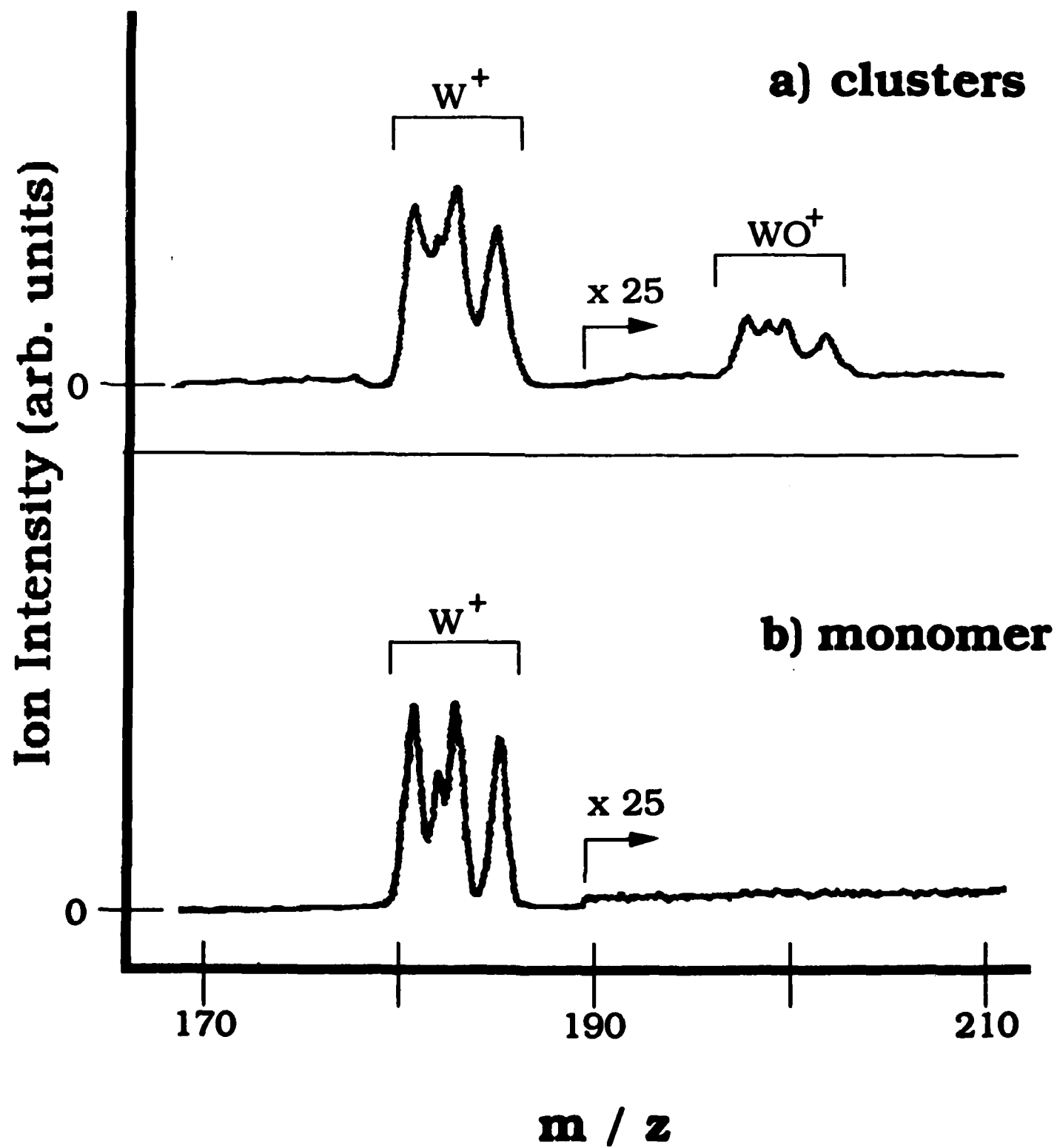


Figure 5. (A) MPI mass spectrum of Cr(CO)_8 van der Waals clusters, 50-150 amu. Signal due to ions of $m/z \geq 60$ amu is amplified by a factor of 2.5. (B) MPI mass spectrum of the unclustered Cr(CO)_8 , 50-150 amu, shown for comparison. As above, ion signal is amplified by a factor of 2.5 for ions of $m/z \geq 60$. Note the exclusive domination of both spectra by the metal ion signal, and the complete absence of metal oxide ions in the mass spectrum of the clusters.

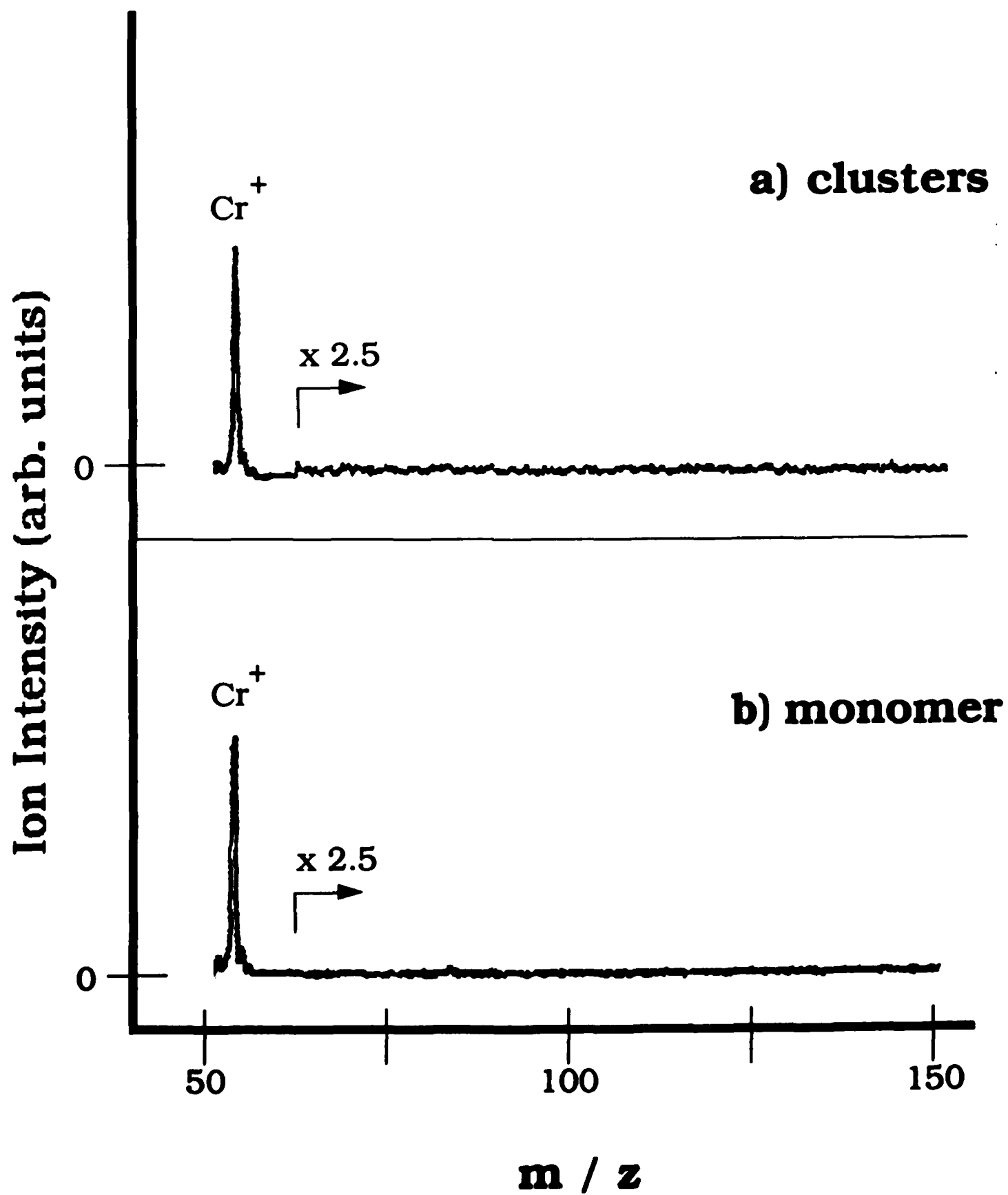


Figure 6. One possible structure for the product of a clustering reaction between a ground-state Cr atom and a neighboring $\text{Cr}(\text{CO})_6$ molecule following multiphoton excitation of a $\text{Cr}(\text{CO})_6$ van der Waals cluster. Clustering between the nascent atom and a coordinatively unsaturated chromium carbonyl would presumably result in a structure with some degree of metal-metal bond character.

