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Wavelength Dependence of the Multiphoton Ionization and Fragmentation Dynamics of $Cr(CO)_6$/Methanol van der Waals Heteroclusters

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Abstract

Mixed van der Waals clusters of $Cr(CO)_6$ and methanol, generated in a pulsed free-jet expansion of seeded helium, are irradiated by strongly focused UV laser pulses, corresponding to intensities on the order of 10^{12} to 10^{13} W/cm^2. Photoions created via multiphoton dissociation (MPD) and ionization (MPI) of these neutral clusters are analyzed by time-of-flight mass spectrometry. We find that the multiphoton dissociation and ionization dynamics of $Cr(CO)_6$ within van der Waals clusters are *quite unusual* in comparison to those of the naked molecule, since the observed photoion yields are highly wavelength dependent, and since complete ligand stripping does *not* appear to dominate the photophysics in the neutral ladder. The observed photoions are accounted for in terms of a dynamical scheme wherein the solvated $Cr(CO)_6$ first undergoes single-photon photodissociation, yielding a solvated coordinatively unsaturated photoproduct, $S_nCr(CO)_x$. The extent of unsaturation in the primary photoproduct is dependent on photon energy, analogous to gas-phase photodissociation of naked $Cr(CO)_6$. This neutral species subsequently undergoes MPI, giving rise to a nascent parent cluster ion, $S_nCr(CO)_x^+$. If this parent cluster ion is sufficiently excited, it can relax to a distribution of daughter ions by at least three different mechanisms: further ligand loss; intracluster bimolecular reaction with an adjacent solvent molecule, leading to a more thermodynamically stable product;

or intracluster V-V energy transfer to the solvent bath. The first of these three alternatives appears to be the dominant energy disposal channel following MPI at 248 nm, while the second of these three alternatives appears to dominate following MPI at 350 nm. CD_3OD is apparently more efficient than CH_3OH in cooling the various photoions via intracluster V-V energy transfer. This may be due to a more favorable correlation of vibrational frequencies and symmetries. Our ability to prepare and spectroscopically interrogate *specific* chromium carbonyl species within van der Waals clusters holds promise as a general technique for probing the electronic structures of coordinatively unsaturated organometallic complexes.

Introduction

Coordinatively unsaturated transition metal carbonyls are of fundamental significance in organometallic chemistry.[1] Many of these species are thought to be intermediates in industrially important catalytic cycles.[2,3] These highly reactive molecules can be synthesized conveniently in the gas phase by pulsed UV laser photolysis of stable, saturated transition metal carbonyls. Mono-unsaturated species can be easily generated in condensed phases by UV or near-UV single-photon photodissociation of saturated precursors.[4] Photodissociation of saturated transition metal coordination compounds in solution, and subsequent coordination of a solvent molecule to the unsaturated photoproduct, occurs on the picosecond timescale.[5] The dynamics of these solution-phase processes have been studied by a variety of transient visible,[6-8] IR,[9-11] and Raman[12] spectroscopic techniques. One would also like to be able to study coordinatively unsaturated molecules in an environment free from energy transfer to and/or reactions with solvent molecules, preferably under collisionless conditions. Although powerful mass spectrometric techniques have been applied to the study of the structure and reactivity of coordinatively unsaturated *ionic* species in the gas phase,[13-15] studies of the excited electronic states of the corresponding *neutral* species are not as numerous.[16] The photolability of transition metal carbonyls makes their study by UV/visible absorption spectroscopy difficult. Excited-state lifetimes are short, and excited species tend to photodissociate rather efficiently; consequently, absorption bands are quite diffuse.[4] Although some unsaturated metal carbonyls ($Ni(CO)_3$, for example[17]) can be induced to fluoresce, electronically excited metal carbonyls generally relax by non-radiative mechanisms, so fluorescence techniques such as LIF have not enjoyed general applicability in gas-phase experiments. Recent developments in pulsed resonance Raman spectroscopy show promise for the study of excited electronic states of coordinatively unsaturated metal carbonyls, although studies so far have been limited to saturated Group VIB hexacarbonyls in solution.[18]

Resonance-enhanced multiphoton ionization (REMPI) spectroscopy, coupled with mass-resolved photoion or energy-resolved photoelectron detection, has proved a most powerful probe of the spectroscopy of open-shell organic and inorganic transient species.[19] Unfortunately, MPI is generally inapplicable to the study of the electronic structure of naked transition metal carbonyls, since multiphoton absorption leads to complete ligand stripping and subsequent atomic, rather than molecular, ionization.[20] However, the multiphoton dissociation and ionization dynamics of *van der Waals clusters* of transition metal carbonyls may, in general, be strikingly different from that of naked molecules. Wheeler and Duncan have observed novel photoinduced intracluster reactivity which accompanies MPI of mixed van der Waals clusters of $Fe(CO)_5$ and either O_2 or CO_2.[21] We have recently found MPI to be a useful probe of novel bimolecular chemistry which takes place between neutral reactants within van der Waals clusters of some Group VIB hexacarbonyls following excitation at 248 nm.[22,23] We have undertaken the present studies in order to further elucidate the multiphoton photophysics of van der Waals clusters of one particular saturated species, $Cr(CO)_6$. In these experiments, we form mixed clusters containing single molecules of $Cr(CO)_6$ surrounded by solvent molecules of methanol. We then subject these mixed clusters to multiphoton excitation, and interrogate the product photoions by time-of-flight mass spectrometry. As we shall describe below, we find that the solvated $Cr(CO)_6$ molecule does not behave like a naked molecule in the gas phase; that is, complete ligand stripping does not accompany multiphoton excitation. Furthermore, we find that the solvated $Cr(CO)_6$ molecule does not behave as though it were in a condensed-phase environment, since the extent of photodissociation on the neutral ladder, *prior to ionization*, is highly dependent on the photodissociation wavelength. These observations imply that the photodissociation behavior of $Cr(CO)_6$ within van der Waals clusters is intermediate between gas-phase and condensed-phase behavior, and that REMPI may be a useful probe of the electronic structure of cluster-bound transition metal coordination compounds.

Experimental Section

Our experimental apparatus is shown schematically in Figure 1. Details of our pulsed cluster beam source and photoionization mass spectrometer will be published elsewhere.[24] Briefly, helium gas (Linde, 99.995%) at 18 psia is passed first through a trap containing methanol (Fisher, certified A.C.S.) at 300 K, then through a 1/4"-dia. U-tube containing $Cr(CO)_6$ (Aldrich, 99%) at 300 K, and finally into the low-volume stagnation region of a pulsed molecular beam valve (Newport Research Corporation BV-100, equipped with a 0.5-mm dia., 30° conical nozzle). Heteroclusters of $Cr(CO)_6$ and methanol form in the free-jet expansion created as pulses of this gas mixture are expanded adiabatically into the molecular beam chamber. The pulsed cluster beam passes through a skimmer and into the differentially pumped ion source of a time-of-flight mass spectrometer, and its chemical composition and temporal profile may be monitored by a residual gas analyzer (Dycor M200M) as it passes out of the distal aperture of the ion source. Operation of the pulsed valve at about 1 Hz results in maximum pressures in the beam chamber and spectrometer chamber of 3×10^{-6} and 2×10^{-7} Torr, respectively, and minimum pressures between pulses of 8×10^{-7} and 6×10^{-8} Torr, respectively. Clusters inside the ion source are irradiated by a tightly focused output pulse from the photoionization laser (vide infra). Photoions which arise following MPD/MPI of the cluster beam are accelerated in a direction orthogonal to both the laser and molecular beams to a nominal energy of 4.25 keV before passage into the 1.5-m drift tube of the mass spectrometer. A small electric field is applied to a pair of transverse deflector plates located just downstream from the ion source in order to compensate for the forward velocity of the molecular beam. Photoions are detected at the end of the drift tube by a dual microchannelplate detector. For the collection of time-of-flight mass spectra, the signal from this detector is collected and averaged over about 1000 laser shots by a digital storage oscilloscope (LeCroy 9400). For the collection of resonance-enhanced MPI (REMPI) spectra, the detector signal is amplified 20X by a fast preamp (EG&G VT120), and the photoion signal corresponding to a specific ion is collected and averaged by a boxcar averager (EG&G/PAR 4420) while the wavelength of the photoionization laser is slowly stepped, in ca. 1.9 cm^{-1} increments, over its tuning range. REMPI spectra of clusters in the molecular beam are typically collected over a period of about twelve hours, corresponding to the mass-resolved photoion signal from about 40,000 laser shots.

For the collection of time-of-flight mass spectra at 248 nm, we used a KrF excimer laser (Lambda Physik EMG-150) which produces typical pulse energies of about 150 to 200 millijoules. Pulses are stopped down to a 3-mm cross sectional diameter, then tightly focused into the center of the ion source by an S1-UV lens of 250-mm focal length (ESCO Products) to an estimated intensity of about 3 or 4 x 10^{12} W/cm^2. For the collection of both REMPI and time-of-flight mass spectra at wavelengths between 346 and 377 nm, we used an excimer-pumped dye laser (Lambda Physik FL-3002, pumped by an EMG 102). The laser dye used (DMQ; Lambda Physik LC 3590) lases with greatest intensity at

360 nm, and has an efficiency of 8.5%. In our experiment, output pulses from this laser are expanded to a 15-mm cross sectional diameter (in order to minimize damage to the external optics), steered as necessary, and tightly focused into the ion source by the 250-mm S1-UV lens described above, resulting in an estimated intensity (depending on wavelength) between about 2 x 10^{12} and 1 x 10^{13} W/cm^2.

In order to simplify the interpretation of mass spectra and to eliminate problems due to isobaric interferences, we also collected mass spectra of heteroclusters of $Cr(CO)_6$ and methanol-d_4 (Aldrich, 99.5 atom % D), as well as REMPI spectra of specific photoions resulting from irradiation of these heteroclusters. We verified mass spectrometrically that no isotopic cross-contamination of the cluster beam was taking place when we switched between CH_3OH and CD_3OD. We were only able to detect a *single* series of homogeneous cluster ions, whose empirical formula is either $(CH_3OH)_nH^+$ or $(CD_3OD)_nD^+$. We never detected both series in the same mass spectrum, nor did we detect any isotopically mixed variants, even for cluster ions containing several dozen molecules. In order to prevent contamination of the molecular beam, the helium buffer gas was purified before seeding by passage through an O_2 and H_2O scrubber (Matheson 6406), and the CH_3OH was purified according to literature methods.[25,26] The CD_3OD was purchased in sealed glass ampules and was used without any further purification, except for degassing. The $Cr(CO)_6$ was purified by sublimation and stored in a sealed manifold under helium.

Results and Discussion

Photoion Yields Following MPI at 248 nm. Portions of the time-of-flight mass spectra of $Cr(CO)_6/CH_3OH$ and $Cr(CO)_6/CD_3OD$ heteroclusters, following MPI at 248 nm, are shown in Figures 2a and 2b, respectively. Although photoions lighter than ca. m/z = 140 are not shown in the portions of the mass spectra illustrated, we *do* see high yields of Cr^+, as well as much smaller yields of the protonated (or deuterated) homogeneous cluster ions $S_n(H/D)^+$ (where S is a methanol or methanol-d_4 molecule), in both spectra. If the multiphoton dissociation and ionization dynamics of $Cr(CO)_6$-containing heteroclusters were rigorously analogous to those of naked $Cr(CO)_6$, one might expect the mass spectrum at the high laser intensities used here to consist primarily, perhaps exclusively, of solvated chromium ions, S_nCr^+. However, while such a sequence of cluster ion peaks is in fact observed in both mass spectra, it is *not* the only sequence we observe. That is, the multiphoton photophysics of solvated $Cr(CO)_6$, in striking contrast to that of naked $Cr(CO)_6$, is *not* characterized by complete ligand stripping. Instead, we observe additional sequences of photoion peaks in the two spectra. Another major sequence observed in these spectra is attributed to cluster ions having the empirical formula, $S_nCr(H_2O)^+$ (or $S_nCr(D_2O)^+$, for S = CD_3OD). This sequence is not seen at intermediate laser fluences (e.g., 10^7 to 10^8 W/cm^2), and may possibly be indicative of an intracluster reaction between two methanol molecules which is mediated by an *electronically excited* chromium ion.[27] Two additional sequences of photoions are observed in the mass spectra: one sequence, corresponding to cluster ions with the formula, $S_nCr(CO)^+$ ($n \geq 4$); and a second, corresponding to cluster ions with the formula, $S_nCr(CO)_2^+$ ($n \geq 5$).

These sequences, $S_nCr(CO)^+$ and $S_nCr(CO)_2^+$, represent only a minor contribution to the total photoion yield in the mass spectrum of $Cr(CO)_6/CH_3OH$ heteroclusters; but they represent a *significant* contribution to the total photoion yield in the mass spectrum of the perdeuterated heteroclusters, as seen from a comparison of Figures 2a and 2b. We offer the following explanation to account for this difference. Suppose that the *primary* photoion is a species, $S_nCr(CO)_x^+$ ($3 \leq x \leq 6$), and suppose further that the ions of formula, S_nCr^+, arise *primarily* by predissociation and/or subsequent photofragmentation of this primary photoion. If the predissociative (or photoexcited) ion can be efficiently cooled by the surrounding solvent molecules, perhaps by intracluster V-V energy transfer, then the tendency for complete ligand stripping can be suppressed, and the yields of species such as $S_nCr(CO)^+$ and $S_nCr(CO)_2^+$ are consequently increased. It is not unreasonable to expect CH_3OH and CD_3OD, because of the differences in their stretching and bending frequencies, to have different efficiencies for relaxation of the internal energy of a coordinatively unsaturated organometallic collision partner. The observed photoion distribution, then, would depend on the chemical identity of the solvent molecules.

Photoion Yields Following MPI Between 350 and 360 nm. A typical time-of-flight mass spectrum resulting from MPI of $Cr(CO)_6/CH_3OH$ heteroclusters at 350 nm is shown in Figure 3a. We note that the cluster ion intensity distribution is not described by a simple exponential decay, but exhibits several maxima and minima; furthermore, the locations of these maxima and minima can be changed simply by changing the magnitude of the transverse deflector field. These maxima and minima arise *not* because of any differences in the relative stabilities of the cluster ions, but rather because of some mechanism which leads to *translationally hot* ions; that is, ions with some non-thermal recoil velocity. This photofragment recoil may result from photodissociation in either the neutral *or* ionic manifold. One of the characteristics of our molecular beam mass spectrometer is that the efficiency for transmission of ions through the drift tube displays a maximum over a limited range of m/z values. This maximum can be shifted to higher or lower values by raising or lowering the magnitude of the transverse deflector field.

Translationally *hot* ions of less-than-optimal m/z will successfully traverse the drift tube if their photofragment recoil vector is aligned parallel to the molecular beam trajectory, and those of greater-than-optimal m/z will likewise traverse the flight tube if their recoil vector is aligned anti-parallel to the molecular beam trajectory. Ion trajectory calculations[28] suggest that with the ion source and transverse deflector biases used for collecting the mass spectrum in Figure 3a, transmission efficiency for ions *with zero recoil* will be greatest for m/z of about 500 amu, and in fact we observe a local maximum at 460 amu. The local maxima observed at about 260 and 690 amu correspond to translationally hot ions whose recoil vectors are about 1.7 eV in magnitude, and are oriented parallel (260 amu) or anti-parallel (690 amu) to the molecular beam.

A representative portion of the 350-nm MPI mass spectrum of $Cr(CO)_6/CH_3OH$ heteroclusters is shown in Figure 3b. Two points are immediately apparent: first, contrary to what one might intuitively expect following MPI of a metal carbonyl, none of the features in this mass spectrum can be attributed to solvated chromium ions, S_nCr^+; and second, the features which *do* appear in the 350-nm MPI mass spectrum are *distinctly different* from those that appear in the 248-nm MPI mass spectrum. This is a significant observation, since it implies that *the multiphoton dissociation and ionization dynamics of* $Cr(CO)_6$ *within van der Waals clusters are wavelength dependent*. This behavior contrasts with that of metal carbonyls dissolved in solution or isolated in cryogenic matrices, where single-photon absorption results in single-ligand loss, independent of wavelength.[5] Because of isobaric interferences from the cluster ions, $(CH_3OH)_nH^+$ and $(CH_3OH)_n(H_2O)H^+$, which appear following non-resonant MPI of homogeneous methanol clusters,[29-31] spectral interpretation based solely on observations from Figure 3b would be tenuous at best. However, based on additional observations from the 350-nm MPI of perdeuterated heteroclusters (vide infra), we can assign with confidence the identities of the cluster ions appearing in the mass spectrum. Three sequences of cluster ions appear: a major sequence, corresponding to ions with the empirical formula, $S_n(H_2O)Cr(CO)_5H^+$ ($n \geq 0$); and two minor sequences, corresponding to ions with the empirical formulas, $S_nCr(CO)_5H^+$ and $S_{n+1}Cr(CO)_4H^+$ ($n \geq 0$). It is not unlikely that the processes leading to the appearance of these protonated or water-containing clusters are intracluster ion-molecule reactions which take place between a nascent chromium carbonyl ion and one or more of the surrounding methanol molecules, *following* the initial photoionization event. Such intracluster processes readily occur in ionized clusters of inorganic and organic molecules.[32]

The 350-nm MPI mass spectrum of $Cr(CO)_6/CD_3OD$ heteroclusters, and an expanded portion of this spectrum, are shown in Figures 4a and 4b, respectively. In this case, the principle sequence corresponds to ions of the empirical formula, $S_nCr(CO)_5D^+$ ($n \geq 0$). Contributions from ions such as S_nD^+ and $S_n(D_2O)D^+$, arising from nonresonant MPI of homogeneous methanol-d_4 clusters, are negligible. Cluster ions corresponding to $S_n(D_2O)Cr(CO)_5D^+$ ($n \geq 0$) are much less abundant than in the case of the CH_3OH-containing heteroclusters, and those containing the $Cr(CO)_4$ moiety are absent altogether. In addition, the intensity distribution of cluster ions in Figure 4a displays a simple monotonic decay, and therefore no evidence of translationally hot photofragment ions. Again, differences between the 350-nm MPI mass spectrum of $Cr(CO)_6/CH_3OH$ heteroclusters (Figure 3a) and that of the $Cr(CO)_6/CD_3OD$ heteroclusters *may* be due to a dynamical effect. Whereas excited organometallic photoproducts may be efficiently cooled by intracluster V-V energy transfer to the solvent bath in the case of CD_3OD-containing clusters, they may perhaps only be cooled by subsequent fragmentation (which may be viewed as V-T energy transfer) or intracluster bimolecular reaction in the case of CH_3OH-containing clusters.

As mentioned earlier, the maximum in the tuning curve of the laser dye used in these experiments is 360 nm. A portion of the 360-nm MPI mass spectrum of $Cr(CO)_6/CD_3OD$ heteroclusters is shown in Figure 4c. This portion of the spectrum spans the same m/z range as the 350-nm spectrum in Figure 4b, but is plotted with a y-axis which is magnified 2.5X. We see that photoions arising from heterocluster MPI have decayed in intensity, while photoions corresponding to S_nD^+ and $S_n(D_2O)D^+$, arising from non-resonant MPI of the homogeneous methanol-d_4 clusters, have dramatically grown in intensity. The fact that the signals corresponding to the heterocluster ions, $S_nCr(CO)_5D^+$ and $S_n(D_2O)Cr(CO)_5D^+$, display intensity maxima at some wavelength *other than* the lasing maximum of the dye suggests that these ions do *not* arise from some non-resonant MPI process, but rather through a *resonance-enhanced* process. The question we must now ask is this: what is the identity of the neutral species which, upon ionization, gives rise to the observed heterocluster ions? In order to address this question, we have examined the REMPI spectra of the various neutral components in our molecular beam. We discuss our results below.

Mass-resolved REMPI Spectra: 346-377 nm. REMPI spectra for several neutral species were collected by monitoring the yields of specific photoions resulting from MPI of the cluster beam at wavelengths between 346 and 377 nm. A few representative spectra are shown in Figures 5a-5c, and a plot of the experimentally measured laser pulse energy versus wavelength is shown in Figure 5d. The REMPI spectra have all been corrected for wavelength-dependent variations in laser intensity, I, using the relation (which is theoretically predicted to hold at the limit of strong focusing and high power densities[33]) that ion signal varies as $I^{3/2}$. This predicted relationship was experimentally verified for Cr^+ yield, but could not be verified for the heavier cluster ions due to signal-to-noise constraints. However, parameterization of the power law and correction based on either a linear, square, or cubic dependence yielded normalized spectra which were qualitatively similar to those shown in Figures 5a-5c. Resonant features which are observed in mass-resolved REMPI spectra are indicative of the electronic structure of the *neutral species* which, upon ionization, gives rise to the *monitored photoion.* Different photofragment ions arising from ionization of the same neutral precursor, *via the same resonant transitions,* will therefore display the same resonant features in their corresponding REMPI spectra.

A REMPI spectrum collected by monitoring the photoion, $Cr(CO)_5D^+$ (which is produced during MPI of the $Cr(CO)_6/CD_3OD$ cluster beam), is shown in Figure 5a. The neutral species which gives rise to this photoion has an absorption maximum somewhere to the blue of 346 nm, outside of the tuning range of the laser dye used. An analogous photoion, $Cr(CO)_5H^+$, should appear following MPI of the $Cr(CO)_6/CH_3OH$ cluster beam, but is obscured by isobaric interference from the much more intense species, $(CH_3OH)_6H^+$. However, it *is* possible to monitor photoions corresponding to the empirical formula, $(CH_3OH)_nCr(CO)_5^+$, which are *not* obscured by isobaric interference from MPI of homogeneous methanol clusters. REMPI spectra collected in such a manner are similar in appearance to each other, regardless of n; furthermore, they display the same resonant feature as the spectrum collected by monitoring $Cr(CO)_5D^+$ (Figure 5a), although the signals for the former are less intense and the signal-to-noise ratios are poorer. All of these photoions -- $Cr(CO)_5D^+$, $S_nCr(CO)_5^+$, and (presumably) $S_nCr(CO)_5H^+$ -- must therefore arise from MPI of *the same neutral precursor*.

The REMPI spectrum collected by monitoring the Cr^+ photoion signal as a function of wavelength is shown in Figure 5b. None of the resonant features in this spectrum are similar to the feature exhibited in the spectrum of Figure 5a, but can instead be assigned to one- and two-photon resonant electronic transitions of neutral chromium atoms. This is further confirmed by our experimental observation that different organochromium precursors (e.g., benzenechromium tricarbonyl) give rise to Cr^+ photoions whose wavelength dependence is identical to that displayed in Figure 5b. A typical REMPI spectrum collected by monitoring the $(CH_3OH)_nH^+$ (n=7) photoion is shown in Figure 5c. Spectra collected by monitoring corresponding ions of different n look identical, and arise due to non-resonant ionization of solvated methanol (followed by a rapid intracluster H-atom transfer reaction). Likewise, these spectra do *not* display the resonant feature exhibited in the spectrum of Figure 5a. Therefore, photoions such as $S_nCr(CO)_5^+$ and $S_nCr(CO)_5(H/D)^+$ *do not arise from MPI of either atomic chromium or solvated methanol*, but arise rather from resonant MPI of some solvated neutral species, $S_nCr(CO)_x$ ($n \geq 1$; x = 5 or 6). Presumably, the photoions of formula $S_nCr(CO)_x$ (x = 0,1,2) which appear following MPI at 248 nm *also* arise from photoionization of some solvated, and perhaps coordinatively unsaturated, chromium carbonyl species.

It seems unlikely that solvated $Cr(CO)_6$ is the neutral precursor which gives rise to the observed photoions at both 248 nm *and* ca. 350 nm. Ionization of $Cr(CO)_6$ to give a $Cr(CO)_6^+$ photoion would require at least two photons at 248 nm, or three photons at 350 nm, and would result in the production of a nascent photoion with as much as 2 eV or 2.6 eV of internal energy, respectively. Subsequent photofragmentation of the parent ion would be expected to occur statistically,[34] and its extent would depend not on the *wavelength* of the MPI laser, but rather on the *total photon energy* absorbed. Consequently, under conditions of strong focusing and high laser intensities, we would expect photoion yields within such a dynamical scheme to be very nearly independent of the wavelength of the MPI laser. Since this expectation runs counter to our results, we must reject the notion that solvated $Cr(CO)_6$ is the neutral precursor of all of the heterocluster photoions observed at both 248 and 350 nm. Similar arguments lead us to reject the notion that a *single* coordinatively unsaturated species (e.g., solvated $Cr(CO)_5$) is the precursor of photoions which arise at both wavelengths. We conclude that irradiation of the heterocluster beam at 248 nm leads to a *different neutral precursor* (or set of precursors) than irradiation at 350 nm, and that differences in the MPI mass spectra (248 nm vs. 350 nm) arise because of the production of *different primary photoions*. Due to the extensive fragmentation which almost *always* occurs when strongly focused laser pulses are used to effect MPI, the degree of coordinative unsaturation of these neutral precursors cannot be *directly* assessed in the present experiments. However, we can make reasonable guesses based on the *known* photodissociation behavior of $Cr(CO)_6$ at 248 and 351 nm.

Photodissociation of $Cr(CO)_6$. The photodissociation behavior of $Cr(CO)_6$ in the gas phase has been well-studied. Results from chemical trapping studies[35] and time-resolved IR spectroscopy experiments[36,37] indicate that absorption of a single 248-nm photon by a $Cr(CO)_6$ molecule results in the loss of two carbonyl ligands and the formation of an excited molecule of $Cr(CO)_4$ with an internal energy of ≤ 38 kcal/mol.[38] On the other hand, absorption of a single 351-nm photon by a $Cr(CO)_6$ molecule results in the loss of a single carbonyl ligand and the formation of an excited molecule of $Cr(CO)_5$ with an internal energy of perhaps as much as 30 to 45 kcal/mol.[39] It seems likely, based on the observed wavelength dependence of photoion yields in our experiments, that such *single-photon* photochemistry is taking place in $Cr(CO)_6$/methanol heteroclusters. We cannot estimate the extent to which secondary photodissociation in the neutral ladder competes with MPI of these primary photoproducts. However, secondary *one-photon* dissociation of these primary photoproducts should occur at a rate linear with laser intensity, while any *multiphoton* process (such as MPI) should occur under conditions of strong focusing and high laser intensity at a rate proportional to $I^{3/2}$. The exponential dependence will deviate even further from linearity (i.e., the value of the exponent will be greater than 3/2) at lower intensities, where geometric saturation does not take place. Depending on the absolute values of the corresponding ionization and photodissociation cross sections, it may be possible to operate in such a regime of laser intensities that MPI of the primary photoproducts dominates over secondary photodissociation.

From the I.P. of $Cr(CO)_6$,[40] the bond dissociation energies of $(CO)_5Cr-CO$ and $(CO)_4Cr-CO$,[41] and the average A.P.'s of $Cr(CO)_x^+$ ($x = 4,5,6$),[42-44] we estimate that the I.P.'s of $Cr(CO)_4$ and $Cr(CO)_5$ are about 7.2 and 7.5 eV, respectively. Photoionization of an internally excited molecule of $Cr(CO)_4$ would require absorption of two 248-nm (5 eV) photons. Photoionization of a *ground-state* molecule of $Cr(CO)_5$ would require absorption of three 350-nm (3.55 eV) photons, although a molecule of $Cr(CO)_5$ with at least 9.2 kcal/mol of internal energy could be two-photon ionized at this wavelength.

Let us assume that the primary *neutral* photoproducts in our cluster experiments are solvated $Cr(CO)_4$ (following 248-nm photolysis) and solvated $Cr(CO)_5$ (following 350-nm photolysis). Further, let us assume that the relevant bond dissociation energies and I.P.'s for the clustered chromium carbonyl species are very nearly equal to the corresponding values for the naked species discussed above. What kind of photoion distribution would we expect to observe following two-photon ionization of excited $Cr(CO)_4$ at 248 nm, or two-photon ionization of excited $Cr(CO)_5$ at 350 nm? Two-photon ionization of excited $Cr(CO)_4$ at 248 nm, assuming dissociative ionization does not take place, should give rise to a nascent $Cr(CO)_4^+$ photoion with as much as 103 kcal/mol of internal energy! A parent ion with this amount internal energy would undoubtedly fragment to smaller daughter ions. Tyndall and Jackson have observed that low-energy electron impact excitation of the nascent $Cr(CO)_4$ product resulting from 248-nm photolysis of $Cr(CO)_6$ in a molecular beam, even at electron energies which are generally too low to effect extensive fragmentation, gives rise to ions of the formula, $Cr(CO)_x^+$ ($x = 0,1,2$).[38] Such extensive fragmentation at low electron impact energies is not surprising, in light of the fact that the internal energy of the neutral $Cr(CO)_4$ is quite high. We might expect, then, that the 248-nm MPI of the nascent, solvated $Cr(CO)_4$ photoproduct in our cluster experiments would also give rise to a distribution of highly unsaturated daughter ions, $S_nCr(CO)_x^+$ ($x < 4$). This expectation agrees well with our observations. On the other hand, two-photon ionization of internally excited (30 to 45 kcal/mol; vide supra) $Cr(CO)_5$ at 350 nm should give rise to a nascent $Cr(CO)_5^+$ photoion with perhaps only 21 to 36 kcal/mol of internal energy. This is probably sufficient for dissociation of only one additional carbonyl ligand from the incipient parent ion. Again, this expectation agrees well with our experimental observations at 350 nm.

Conclusions

We have examined the multiphoton dissociation and ionization dynamics of mixed van der Waals clusters containing single molecules of $Cr(CO)_6$ surrounded by several solvent molecules of methanol. We find that the multiphoton photophysics of these clusters is *not* analogous to that of naked $Cr(CO)_6$ in the gas phase. That is, multiphoton excitation of these heteroclusters is *not* described by a dynamical scheme in which complete ligand stripping takes place initially, followed by photoionization of an atomic metal photoproduct. Instead, we find that a coordinatively unsaturated chromium carbonyl species is created initially within the cluster via single-photon dissociation. Based on the interpretation of our mass spectrometric results, we conclude that irradiation of these clusters at 248 nm gives rise to product clusters containing $Cr(CO)_4$, while irradiation at wavelengths around 350 nm gives rise to product clusters containing $Cr(CO)_5$. This type of dynamical behavior is reminiscent of the single-photon dissociation dynamics of naked $Cr(CO)_6$ in the gas phase. The primary photoproduct subsequently undergoes MPI to give nascent cluster ions of empirical formula, $S_nCr(CO)_x^+$, where x = 4 or 5 for excitation at 248 or 350 nm, respectively. Internally excited nascent ions may relax in one of at least three ways: subsequent ligand loss from the parent ion, ion-molecule reactions with surrounding solvent molecules within the cluster, and intracluster V-V energy transfer to the solvent bath. For the case of 248-nm irradiation, extensive fragmentation of the highly excited nascent parent ions appears to take place, and the observed photoion distribution is dominated by ions of empirical formula, $S_nCr(CO)_x^+$ (x = 0,1,2). For the case of irradiation at wavelengths near 350 nm, the nascent parent ions, $S_nCr(CO)_5^+$, appear to undergo an H-atom (or D-atom) transfer reaction with an adjacent solvent molecule within the cluster, yielding

$S_nCr(CO)_5(H/D)^+$. In general, CD_3OD appears to be more efficient than CH_3OH in cooling the internal energy of an excited $Cr(CO)_x^+$ ion via intracluster V-V energy transfer. Although we are unable to assess the extent of photoinduced evaporation of solvent monomers from the mixed clusters, we suspect that this may be an important mechanism for disposal of excess energy in the cluster ions due to subsequent photon absorption following ionization. Perhaps most importantly, our ability to photolytically prepare and spectroscopically probe van der Waals clusters containing *specific* coordinatively unsaturated organometallic species may allow us to elucidate the electronic structure and chemical reactivity of this important class of molecules.

Acknowledgment

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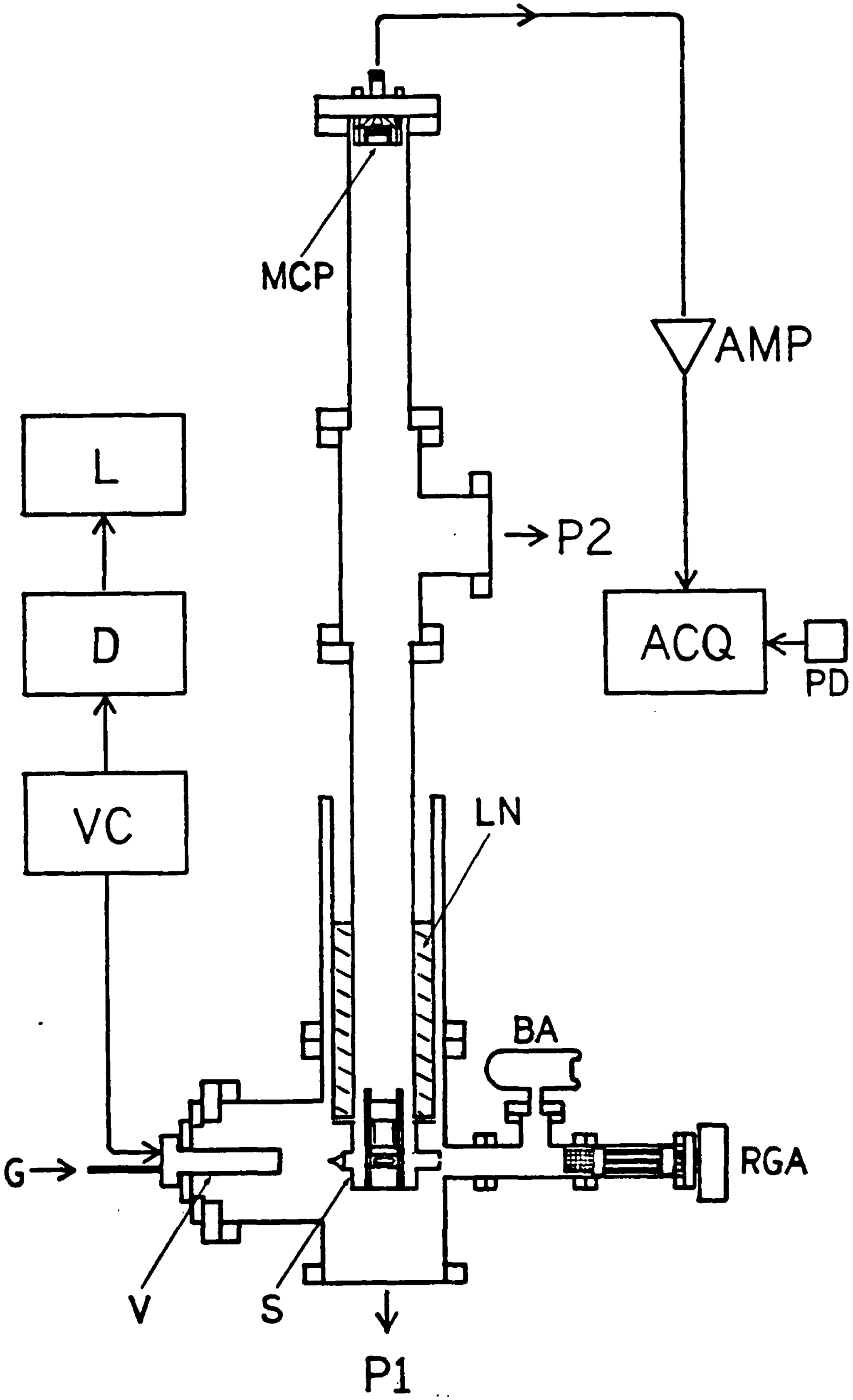
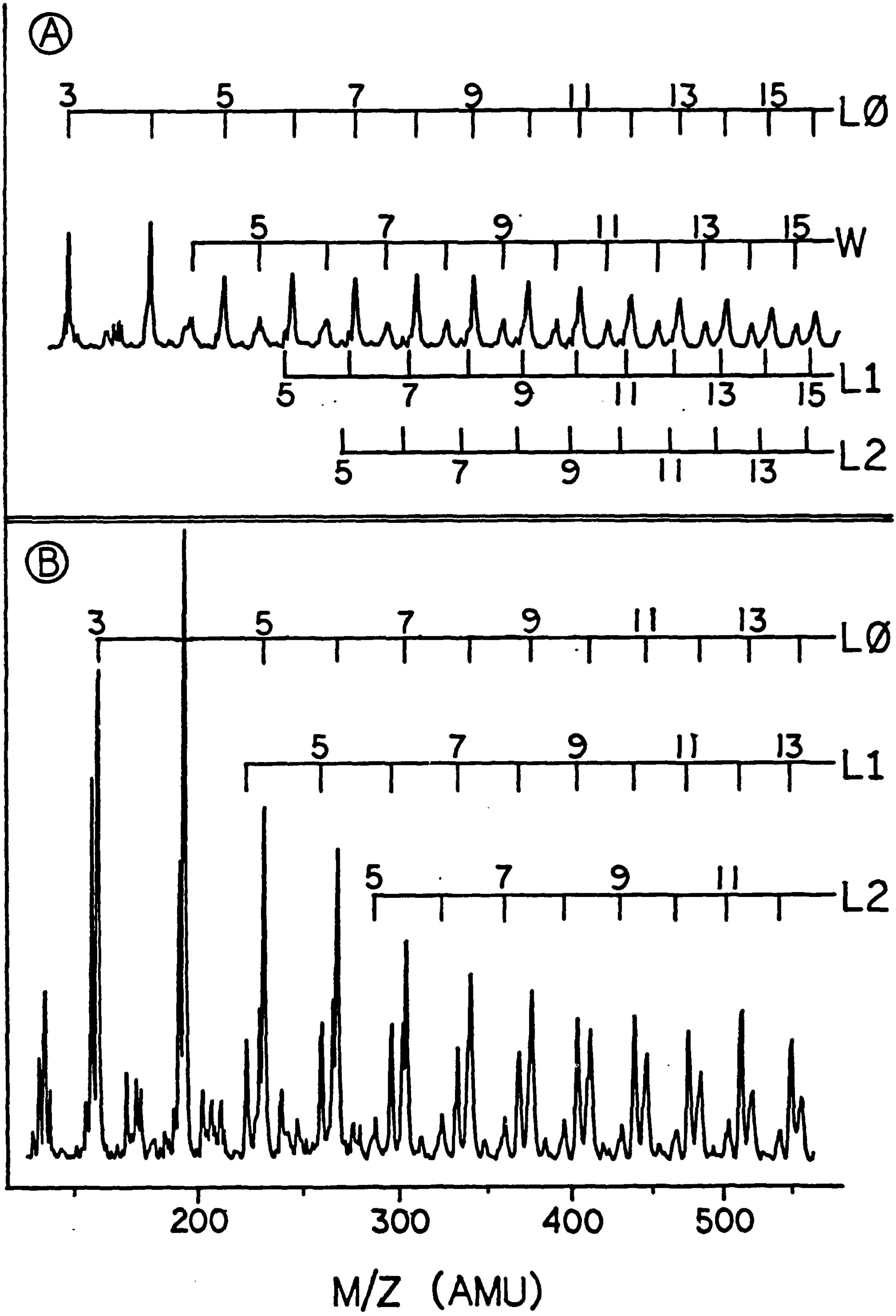
Figure 1. Time-of-flight mass spectrometer, with pulsed molecular beam inlet and photoionization source. Auxiliary apparatus is shown schematically. V -- pulsed molecular beam valve; G -- gas mixture inlet; S -- ion source and shroud (for clarity, molecular beam skimmer/inlet, exit aperture, and laser entrance aperture are not labeled); LN -- liquid nitrogen, used for cooling of ion source shroud and flight tube; MCP -- microchannelplate detector; RGA -- residual gas analyzer, used as molecular beam diagnostic monitor; BA -- Bayard-Alpert ionization gauge tube. The molecular beam chamber is pumped by a 1400-L/sec, 6" A.S.A. oil diffusion pump fitted with a liquid nitrogen-cooled baffle (P1), while the ion source and flight tube are pumped by a 300-L/sec turbopump (P2). The pulsed valve controller (VC), upon receipt of a master timing signal, simultaneously fires the pulsed valve and activates a delayed pulse generator (D). Output from D causes the photoionization laser (L) to fire in coincidence with the skimmed molecular beam pulse. The master timing signal controlling VC may be generated internally (for collection of mass spectra), or received *externally* from the computer which controls the dye laser grating (for collection of REMPI spectra). In either case, the laser pulse impinges upon a fast photodiode (PD) after exiting the ion source, triggering signal collection and averaging by the appropriate data acquisition hardware (ACQ). For the collection of REMPI spectra, raw ion current from MCP is amplified by a fast 20X preamp (AMP) prior to gated detection.

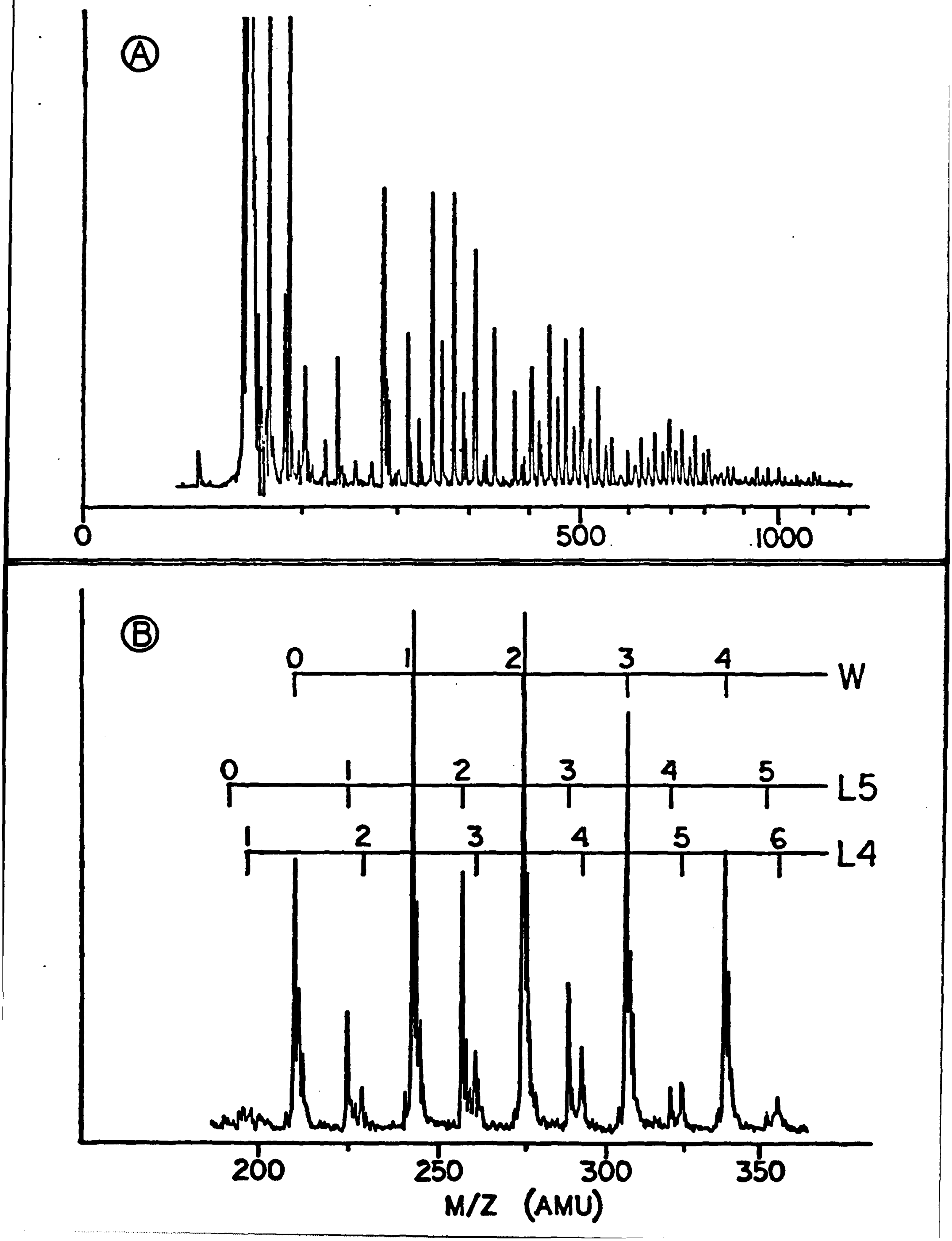


MCP
AMP
L
D
VC
P2
ACQ
PD
LN
BA
G
RGA
V
S
P1

Figure 2. Portions of the 248-nm MPI mass spectra of: (A) $Cr(CO)_6/CH_3OH$ heteroclusters, and (B) $Cr(CO)_6/CD_3OD$ heteroclusters. Spectrum (B) was plotted using a Y-axis scale five-fold more sensitive than that used for Spectrum (A). The mass scale for both spectra is identical and appears at the bottom of the figure. Each of the sequences of cluster ions discussed in the text is identified by a separate horizontal scale. Numbers on each scale represent the number of solvent molecules, S (where S = CH_3OH or CD_3OD), in a given cluster ion. Key: L0 -- S_nCr^+; L1 -- $S_nCr(CO)^+$; L2 -- $S_nCr(CO)_2^+$; W -- $S_nCr(H_2O)^+$. In Spectrum (B), cluster ions corresponding to $(CD_3OD)_nCr(D_2O)^+$ are isobaric with those corresponding to $(CD_3OD)_{n-1}Cr(CO)_2^+$.

A
3
5
7
9
11
13
15
L0
5
7
9
11
13
15
W
5
7
9
11
13
15
L1
5
7
9
11
13
L2
B
3
5
7
9
11
13
L0
5
7
9
11
13
L1
5
7
9
11
L2
200
300
400
500
M/Z (AMU)

<u>Figure 3</u>. (A) 350-nm MPI mass spectrum of $Cr(CO)_6/CH_3OH$ heteroclusters, from m/z = ca. 20 to 1200 amu. Note the maxima located at about 260, 460, and 690 amu (see text). (B) Expanded portion of the 350-nm mass spectrum of $Cr(CO)_6/CH_3OH$ heteroclusters. Cluster ion sequences are labeled using a scheme similar to that used in Figures 2a and 2b. Key: L4 -- $S_nCr(CO)_4H^+$; L5 -- $S_nCr(CO)_5H^+$; W -- $S_n(H_2O)Cr(CO)_5H^+$.



A
0
500
1000
B
0
1
2
3
4
W
0
1
2
3
4
5
L5
1
2
3
4
5
6
L4
200
250
300
350
M/Z (AMU)

Figure 4. (A) 350-nm MPI mass spectrum of $Cr(CO)_6/CD_3OD$ heteroclusters. Note the simple, monotonic decay of cluster ion intensity beyond about 200 amu, and the lack of local maxima as seen in the mass spectrum of the corresponding CH_3OH-containing heteroclusters (cf. Figure 3a). (B) Expanded portion of the 350-nm mass spectrum of $Cr(CO)_6/CD_3OD$ heteroclusters. Again, cluster ion sequences are labeled using the same scheme as in previous figures. Key: L5 -- $S_nCr(CO)_5D^+$; W -- $S_n(D_2O)Cr(CO)_5D^+$; S -- S_nD^+. Note that the sequence of homogeneous cluster ions (sequence S) contributes very little to the total photoion yield following MPI at 350 nm. (C) Expanded portion of the 360-nm mass spectrum of $Cr(CO)_6/CD_3OD$ heteroclusters. This spectrum is plotted using a Y-axis scale which is 2.5 times more sensitive than that of Figure 4b. Here, MPI is accomplished using photons of 360-nm wavelength, the wavelength of maximum dye laser photon flux. Note that the heterocluster ions (sequence L5) now contribute very little to the photoion yield, while the the homogeneous cluster ions (sequence S) are predominant. A new sequence has also appeared: the sequence labeled SW, which corresponds to ions of the formula, $S_n(D_2O)D^+$.

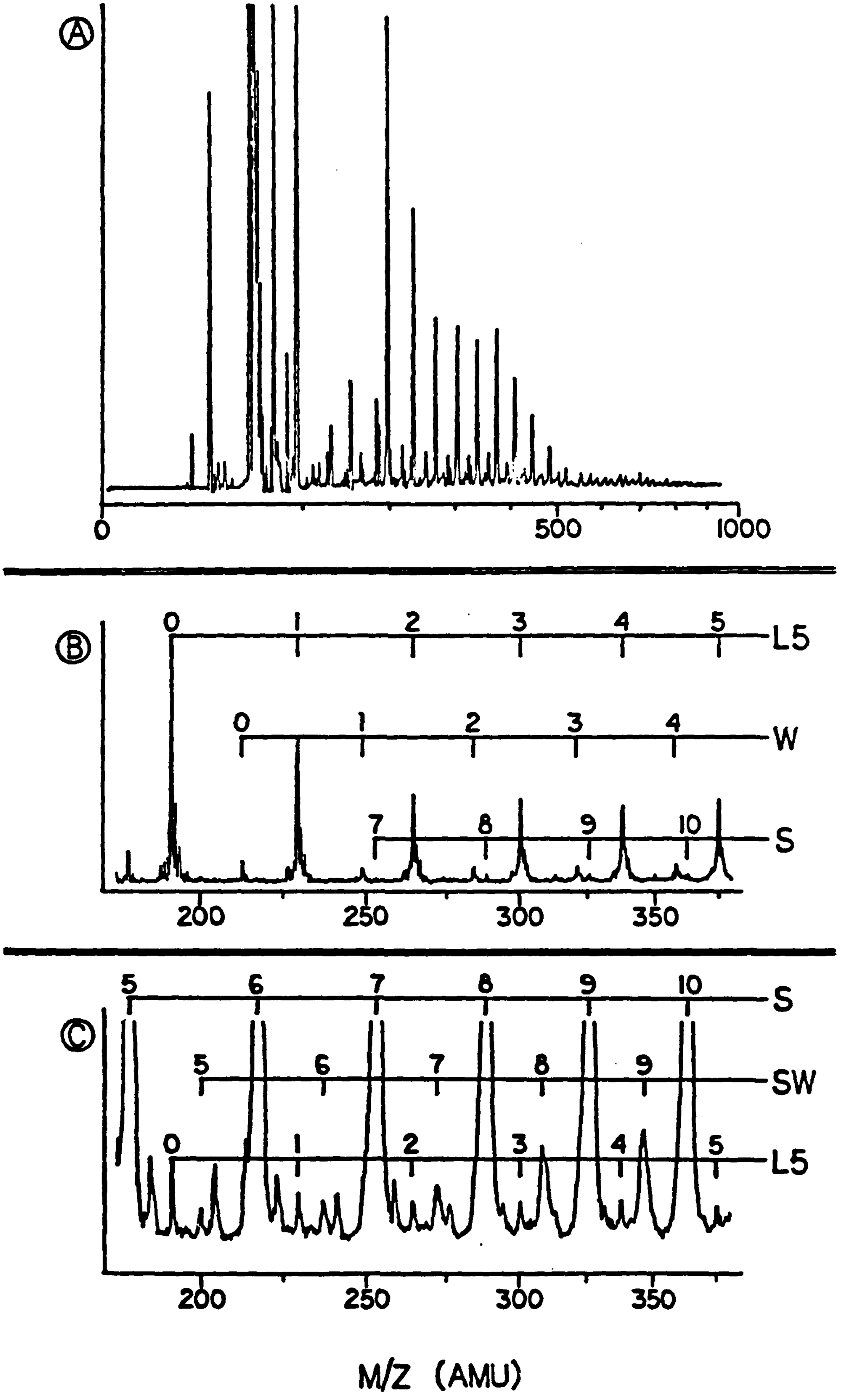
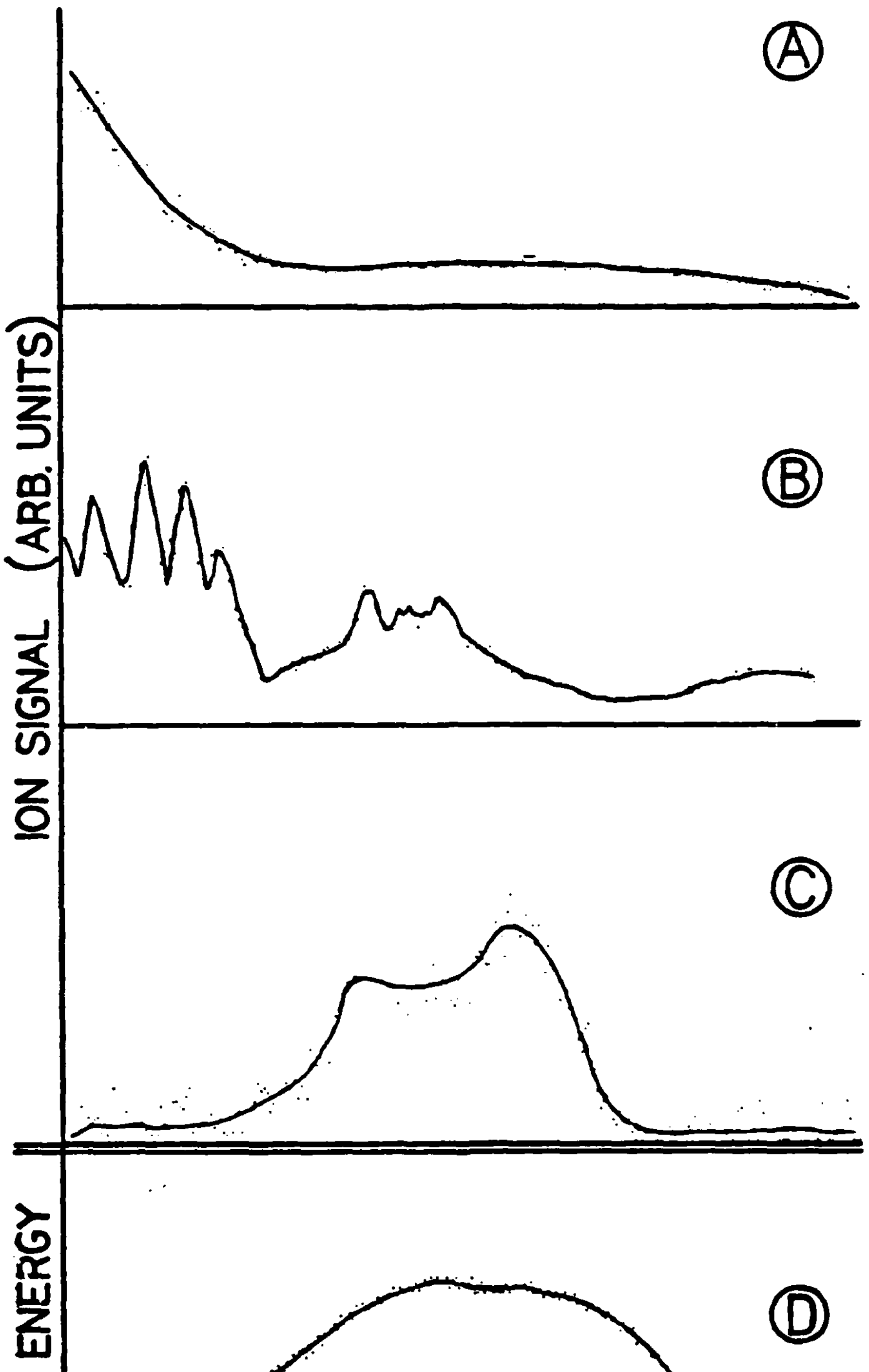

A
0
500
1000
B
0
1
2
3
4
5
L5
0
1
2
3
4
W
7
8
9
10
S
200
250
300
350
C
5
6
7
8
9
10
S
5
6
7
8
9
SW
0
1
2
3
4
5
L5
200
250
300
350
M/Z (AMU)

Figure 5. REMPI spectra of the $Cr(CO)_6$/methanol heterocluster beam. All spectra are corrected for wavelength-dependent variations in laser intensity using the relationship which is predicted to hold under conditions of geometric saturation (see text). (A) $Cr(CO)_5D^+$ signal vs. laser wavelength, produced following MPI of the $Cr(CO)_6/CD_3OD$ cluster beam. Identical spectra result if a $Cr(CO)_6/CH_3OH$ cluster beam is subjected to MPI, and ion signal at m/z = 224 or 448, for example (corresponding to $S{\bullet}Cr(CO)_5^+$ and $S_8Cr(CO)_5^+$), is monitored as a function of wavelength. (B) Cr^+ signal vs. laser wavelength, produced following MPI of the $Cr(CO)_6/CH_3OH$ cluster beam. Spectra collected following MPI of either the $Cr(CO)_6/CD_3OD$ cluster beam, or a static sample of $Cr(CO)_6$, are identical to the one illustrated here. Spectral features are due to one- and two-photon resonant transitions between electronic states of neutral atomic Cr. (C) $(CH_3OH)_7H^+$ signal vs. laser wavelength, produced following MPI of the $Cr(CO)_6/CH_3OH$ cluster beam. Spectra collected by monitoring cluster ion signal, S_nH^+, for values of n other than 7 are similar, although not all such spectra show the depletion of ion signal around 358-362 nm. This depletion *may* be due to enhanced fragmentation of the cluster ions at wavelengths near the dye laser output maximum at 360 nm. (D) Experimentally measured dye laser intensity vs. wavelength.


Ⓐ
Ⓑ
Ⓒ
Ⓓ
ION SIGNAL (ARB. UNITS)
PULSE ENERGY
350
355
360
365
370
375
λ (NM)