vectors, but the r^{-6} dependence of the NOE the problem of spin diffusion[10] precluded quantitation of the distance between the Val-Orn-Leu strands. HX rates,[7,13,68] NMR chemical shift temperature coefficients,[2,68] and the solvent variation of NMR chemical shifts[2,12] were not definitive, since all were equally consistent with transannular H-bonding or steric shielding of Val and Leu NH from bulk solvent. Consequently, the important question of whether the conformation was constrained by one or two pairs of intramolecular H-bonds[79] remained, until the present study, unsettled.

In peptides less thoroughly investigated than GrS, the identification of specific intramolecular H-bonds by vibrational spectroscopy should clearly provide a powerful constraint in conformational analysis. We have shown that the IR spectrum of a peptide bond thus isolated readily furnishes information concerning the structure and energetics of the H-bond not obtainable by methods conventionally employed with polypeptides. Thus, the experimental protocol outlined here should form a basis for the systematic study of the role of intramolecular H-bonding in the stabilization of polypeptide conformation. GrS, which possesses two types of H-bond known to be ubiquitous in peptides and proteins,[80] one typical of β sheets and the other of $4\rightarrow1$ reverse turns, may prove a very useful prototype in this endeavor.

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Multiphoton Ionization Time-of-Flight Mass Spectrometry of Transition-Metal Complexes: Mn₂(CO)₁₀ and Re₂(CO)₁₀

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Abstract: Pulsed laser irradiation of gas-phase Mn₂(CO)₁₀ at selected wavelengths (e.g., 511 and 483 nm) induces extensive photofragmentation, followed by multiphoton ionization of the Mn, Mn₂, and MnCO photoproducts. Subsequent ion–molecule reactions of MPI-generated Mn⁺ with Mn₂(CO)₁₀ ($\sim 10^{-5}$ torr) and Re₂(CO)₁₀ ($\sim 10^{-6}$ torr) yield adduct ions Mn₃(CO)₁₀⁺ and MnRe₂(CO)₁₀⁺ and their daughter ions.

The challenge of understanding a new class of molecules, i.e., complexes containing transition-metal cores, with potential practical applications has prompted a grat deal of activity by organometallic chemists in the areas of synthesis and characterization.[1] The rich photochemistry of these compounds[2] presents interesting problems concerning their photofragmentation and the spectroscopy of the resulting fragments. The lack of detailed gas-phase experimental data has hindered the development of a theoretical picture of bonding in these compounds.[3]

Recently, methods for the study of photofragmentation and photoionization of isolated molecules have become available. For example, resonance enhanced multiphoton ionization (REMPI) studies[4,5] have been successfully applied to a variety of polyatomic organic molecules. The process observed consists of concerted absorption of several photons to a resonant intermediate electronic state of the molecule followed by absorption of additional photons to produce ionization and then fragmentation. However, recent gas-phase multiphoton ionization (MPI) experiments[6,7] on transition-metal compounds indicate that excitation of these molecules results in efficient photofragmentation followed by ionization of the neutral photoproducts.

The present paper reports MPI-mass spectrometry of transition-metal complexes aimed at elucidating their photodissociation, photoionization, and the gas-phase chemistry of resulting photofragments. The model system M₂(CO)₁₀ (M = Mn and Re)

chosen exemplifies transition-metal complexes containing metal–metal bonds.[2] Most of the experimental information to date on the photochemistry of these molecules comes from condensed-phase experiments. Kinetic studies in solution[7] identify M–M homolytic cleavage as the first step in the light-initiated solution chemistry of M₂(CO)₁₀. In the vapor phase, luminescence after UV laser photodissociation of Mn₂(CO)₁₀ has been observed.[8]

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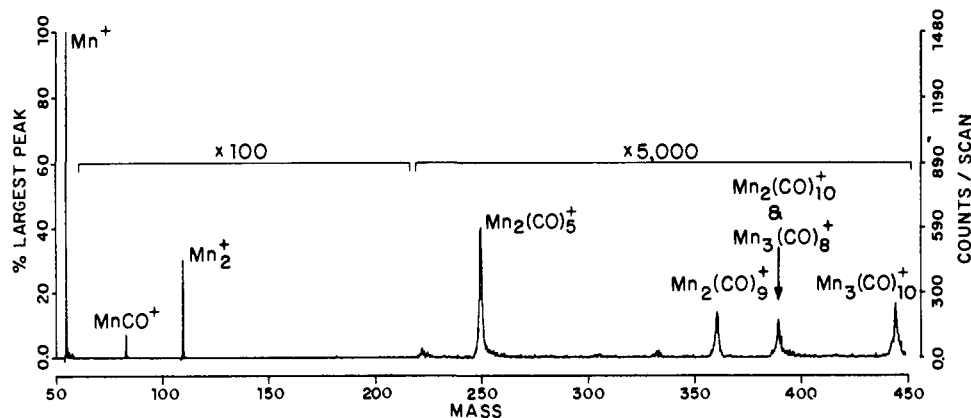(7) Z. Karny, R. Naaman, and R. N. Zare, *Chem. Phys. Lett.*, **59**, 33 (1978).

Figure 1. MPI mass spectrum of $Mn_2(CO)_{10}$ (1.0×10^{-5} torr), produced by 9-mJ laser pulses at 511.1 nm. Broad peaks at high masses (e.g., ca. 250 amu) are attributed to bimolecular ion-molecule reaction products (see text).

It has been shown[9] that Re–Re fission is the first step in the photodissociation of $Re_2(CO)_{10}$ in a molecular beam. In the gas-phase, multiphoton excitation of $Mn_2(CO)_{10}$ over a broad range of wavelengths leads to efficient dissociation to bare Mn atoms,[10] occurring via a sequential mechanism.

The present study consists of multiphoton dissociation (MPD) of gas-phase $M_2(CO)_{10}$ (M = Mn and Re), followed by mass selective detection of the photoionized fragments.

Experimental Section

The experiments were carried out in a laser time-of-flight mass spectrometer (LTOFMS), whose features have been previously described.[4b,c] The inlet system has been modified to include a second, "direct inlet" for use with low vapor pressure samples. This arrangement consists of a shutoff valve, a needle-tpye regulator valve, and a $^1/_4$-in. stainless steel tubing connector between the sample vial and the ionization chamber. For reactions involving $Mn_2(CO)_{10}$ amd $Re_2(CO)_{10}$, the former was introduced via the original molecular leak inlet and the latter through the new inlet, thus providing independent pressure control. Background pressures were 4×10^{-7} torr in the ionization region chamber and 7×10^{-8} torr in the drift tube. Pressures in the ionization region of the bimetallic carbonyl compounds were limited by the (room temperature) rate of sublimation for the molecules. Pressures were measured by using air-calibrated Bayard-Alpert ionization gauges. Therefore the nominal pressures reported, while they are linearly proportional to the pressure for a given compound, are only upper limits for the true pressure.

One key feature of our LTOFMS is the ability to vary the time between the laser pulse and the application of the ion drawout pulse which determines the zero of the time-of-flight mass analysis. This delay (-0.7–$+7$ μs) was normally set at 1.5 μs for investigation of reaction products. This time corresponds to that needed for correct "focusing"[11] of ions in the mass range of interest when they are formed via conventional electron impact (70-eV EI) ionization.

EI mass spectra of all samples were recorded before or after all MPI data collection to check for impurities. Essentially perfect agreement was found between the EI mass spectra and the literature.[15] The EI mass spectra verified the usual unit mass resolution of the instrument for masses up to 400 amu. Any broadening of mass peaks for the MPI-generated ions is therefore due to the intrinsic nature of the processes under observation (see Results).

For all experiments, the laser used was a Quanta-Ray ND:YAG pumped dye laser (model PDL-1), with a 5-ns pulse duration. While various laser beam focusing conditions were investigated, for all results discussed below, a 0.25-m f.l. spherical lens was positioned to focus in the ionization region. In contrast to EI where pyrolysis can take place on the hot filament, MPI spectra were taken with the filament cold, so

no thermal decomposition of the carbonyls is expected to occur.

Results

As anticipated,[10] for both metal carbonyls investigated, the main ion fragment observed was the metal atomic ion. However, M_2^+ was also observed at much lower signal levels. In the case of $Mn_2(CO)_{10}$, where the sample pressure was high enough to allow detection of less prominent peaks, $MnCO^+$ was also observed. While CO^+ was often a major component of the total ion signal from EI on these compounds, it was never observed with MPI.

Lowering of the laser fluence decreased the total ion signal but yielded no decrease in fragmentation, i.e., increase in the relative contribution from larger fragments, in contrast to expectations for a conventional MPI fragmentation process.[12] This result is indicative of a sequential process: dissociation being the initial step, followed by MPI of the resultant neutral fragments. By tuning the laser to a known two-photon transition of the metal atom,[10,13] resonance enhancement was observed for ions derived from the neutral metal atom (see below). As expected, the resonance enhancement decreased as the laser fluence was increased, as higher order multiphoton processes became predominant.

Due to its relatively high vapor pressure, $Mn_2(CO)_{10}$ was the compound investigated in more detail. A typical MPI mass spectrum is shown in Figure 1. Besides the three above-mentioned ions (M^+, M_2^+, MCO^+) which produce sharp mass peaks, broad peaks are observed at higher masses. This broadening could be caused by at least three effects: (1) ion formation and/or destruction during the period of the ion drawout pulse, (2) ion formation with high translational energy and (3) ion formation over a large volume of space. On the basis of data presented below, it is believed that while the sharp peaks are due to MPI of neutral fragments from MPD of the parent molecule, the broadened peaks result from reactions between the copious MPI-generated Mn^+ ions and parent $Mn_2(CO)_{10}$ molecules.

The most striking evidence for reaction is the presence of a broad peak beyond the parent mass (390 amu) at m/e 445. This "superparent" peak corresponding to $Mn_3(CO)_{10}^+$ could only be formed via reaction. EI spectra in the same region reveal a similarly wide peak, two orders of magnitude smaller than the sharp parent peak. It can be assumed that this ion is formed via the same reaction involving EI-formed Mn^+ ions.

Pressure dependence studies were made for all the major peaks; the results are shown in Figure 2. Data on weak peaks have been excluded from analysis (e.g., ca. 334 amu of $Mn_2(CO)_4^+$). For direct ionization (of Mn, MnCO, and Mn_2), a linear dependence upon $Mn_2(CO)_{10}$ pressure is observed. Those fragments resulting from the reaction of Mn^+ with $Mn_2(CO)_{10}$ show quadratic dependence.

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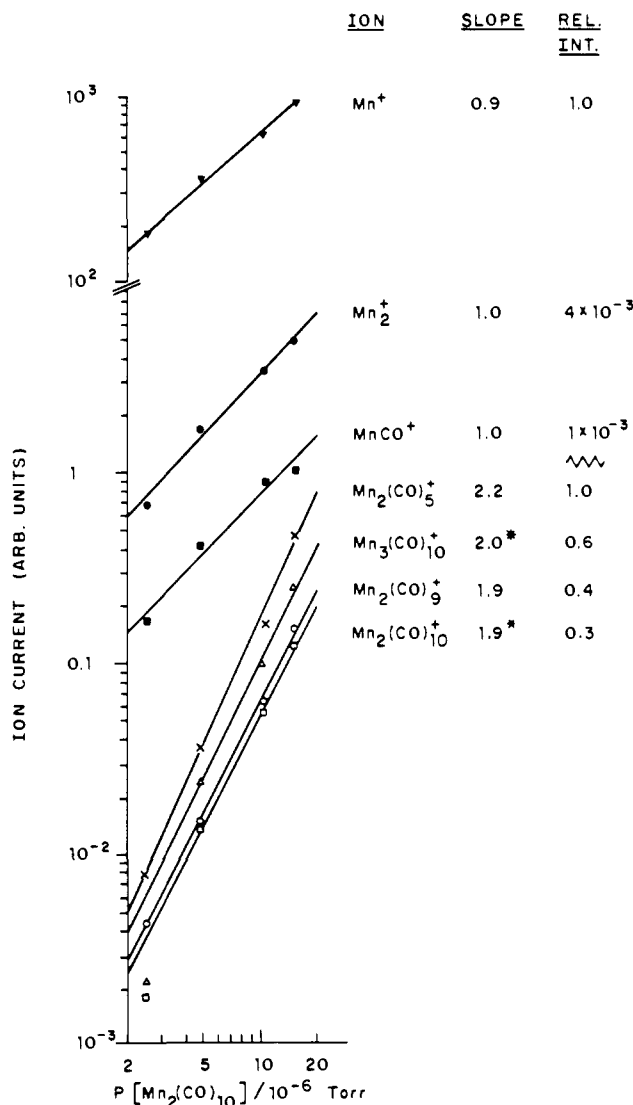
Figure 2. Log–log plot of ion peak intensity vs. nominal sample pressure, when irradiating $Mn_2(CO)_{10}$ with 5-mJ laser pulses at 511.1 nm. Intensities were determined from the area under the mass peaks (defined as ranging from −5 to +15 amu from the nominal mass). First-order pressure dependence is noted for direct ionization peaks Mn^+ (▼), Mn^{2+} (●), and $MnCO^+$ (■). Second-order dependence is found for all broad peaks; $Mn_2(CO)_5^+$ (x), $Mn_2(CO)_9^+$ (O), $Mn_2(CO)_{10}^+$ (□), and $Mn_3(CO)_{10}^+$ (△). Listed is the least-squares-fit slope for each fragment (* indicates that the lowest pressure data point was omitted for the fit). Also listed are the relative intensities of the peaks at 1×10^{-5} torr, with the direct ionization peaks being compared to Mn^+, and the bimolecular reaction products compared to $Mn_2(CO)_5^+$.

Due to the broad mass peaks of these "reaction products" one is unable to differentiate between Mn (55 amu) and $(CO)_2$ (56 amu) in "high mass" ions. This uncertainty makes somewhat equivocal the assigned composition of a few of the product ions.

To obtain additional evidence for the ion–molecule reaction mechanism, experiments were carried out with a 1:10 mixture of $Re_2(CO)_{10}$ in $Mn_2(CO)_{10}$ at a wavelength (511.1 nm) that yields resonance-enhanced production of Mn^+. Comparing the spectra taken before (Figure 3) and after (Figure 4) the addition of the $Mn_2(CO)_{10}$ to the $Re_2(CO)_{10}$, dramatic differences are seen. With $Re_2(CO)_{10}$ alone, the observed signal is from Re^+, Re_2^+, and a small background of fragment ions from trace residual $Mn_2(CO)_{10}$. No ions were observed above mass 450; data (not shown) ranged up to m/e 750 amu. When $Mn_2(CO)_{10}$ was introduced into the ionization chamber, all peaks observed in spectra of the individual compounds are found. However, additional ions are observed with masses in the range 460–750 amu. These additional broad peaks are identified as $Mn^+ + Re_2(CO)_{10}$ reaction products. The peak

centered at 707 amu is assigned to $MnRe_2(CO)_{10}^+$ and that at 652 amu to $MnRe_2(CO)_8^+$ (though the latter could possibly be $Re_2(CO)_{10}^+$ if charge transfer were occurring). There is a weak peak between these two major product peaks which could be $MnRe_2(CO)_9^+$ or could arise from disintegration of the "superparent" during the ion drawout pulse. This latter process is probably the source of most of the "noise" in the spectra. The intensities of peaks assigned to products of the reaction of Mn^+ with $Re_2(CO)_{10}$ (the latter at constant pressure) varied linearly with $Mn_2(CO)_{10}$ pressure.

Data have also been acquired on the laser power dependence of the various direct ionization and reaction product fragments. Results both on and off the Mn 511.1-nm atomic resonance indicate that the yield of Mn^+, its reaction products, and $MnCO^+$ are roughly proportional to the laser pulse energy squared, while the production of Mn_2^+ has a near-linear dependence.

Besides 511.1 nm, experiments were run at 483.0 and 648.7 nm. Irradiation with 483.0-nm light, which couples with the a^6S ground state for resonance enhancement (rather than that the a^6D state at 511.1 nm[10,13]), produced ca. 10 times as much Mn^+. The intensity of this signal indicates ca. 20% conversion of Mn (from all sources) to Mn^+ within the ionization volume.

The experiments at 648.7 nm selectively produced (via REMPI) Mn_2^+ from the neutral Mn_2 photofragment.[14] Though the Mn_2^+ ion peak was ca. 20 times stronger relative to Mn^+ at this wavelength than at 511.1 nm, it was still only ca. 10% of a total signal (mainly Mn^+) which was ca. 10^3 times smaller (most likely due to less efficient MPD at this wavelength). Thus, the amount of Mn_2^+ present was insufficient to yield observable ion–molecule reaction products.

Discussion

REMPI experiments on polyatomic organic molecules[4,5] establish that extensive fragmentation takes place by processes such as ladder climbing through the resonant states past the ionization potential of the molecule, followed by photofragmentation of the parent ion. However, UV–VIS excitation of transition-metal carbonyls leads to a very different course for ionization.[6,7] Typical of all carbonyls, MPI studies on $Mn_2(CO)_{10}$ identify Mn^+ as the major photofragment produced following laser excitation.[10] The structured spectrum of total ion current as a function of wavelength has been assigned to one- and two-photon resonances originating in the ground and excited states of the Mn atom. These MPI experiments on transition-metal carbonyls suggest that multiphoton absorption is occurring to a resonant state which dissociates rapidly by loss of CO ligands. Sequential loss of the ligand leads to metal atoms (reaction 1), which are subsequently multiphoton ionized

$$M_2(CO)_{10} \xrightarrow{n_1 h\nu} \text{intermediates} \xrightarrow{n_2 h\nu} M \qquad (1)$$

(reaction 2). The appearance potential[15] for Mn^+ from Mn_2-

$$M \xrightarrow{n_3 h\nu} M^* \xrightarrow{n_4 h\nu} M^+ \qquad (2)$$

$(CO)_{10}$ is 22.1 eV (that of Re^+ is 30.9 eV) so that at 511.1 nm a total of at least 9 photons (or 13 photons for $Re_2(CO)_{10}$!) are required to form Mn^+, Mn, and 10(CO). At this wavelength, six photons are presumably involved in the photodissociation step; two photons are necessary to achieve the $a^6D \rightarrow i^6D$ transition observed for Mn at 511.1 nm, and an additional photon ionizes Mn^*.

In the present study TOF spectra of multiphoton-ionized molecules were produced at several laser wavelengths. Signal enhancement is observed for M^+ ions when the laser is tuned to an atomic transition. This implies that dissociation to neutral photofragments is the primary step in the multiphoton dissociation of $M_2(CO)_{10}$.

As shown in Figures 1 and 3, irradiation of $M_2(CO)_{10}$ at 511.1 nm yields a distribution of ions. According to the discussion above

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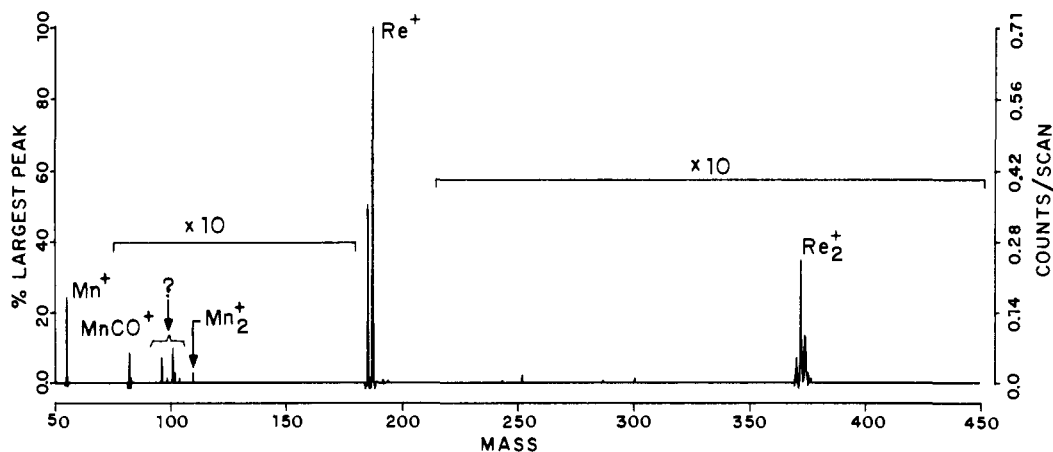(15) H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 2836 (1967).

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Figure 3. MPI mass spectrum of $Re_2(CO)_{10}$ (2.6×10^{-6} torr), using 7.5-mJ laser pulses at 511.1 nm. No peaks were observed at higher mass (up to 750 amu).
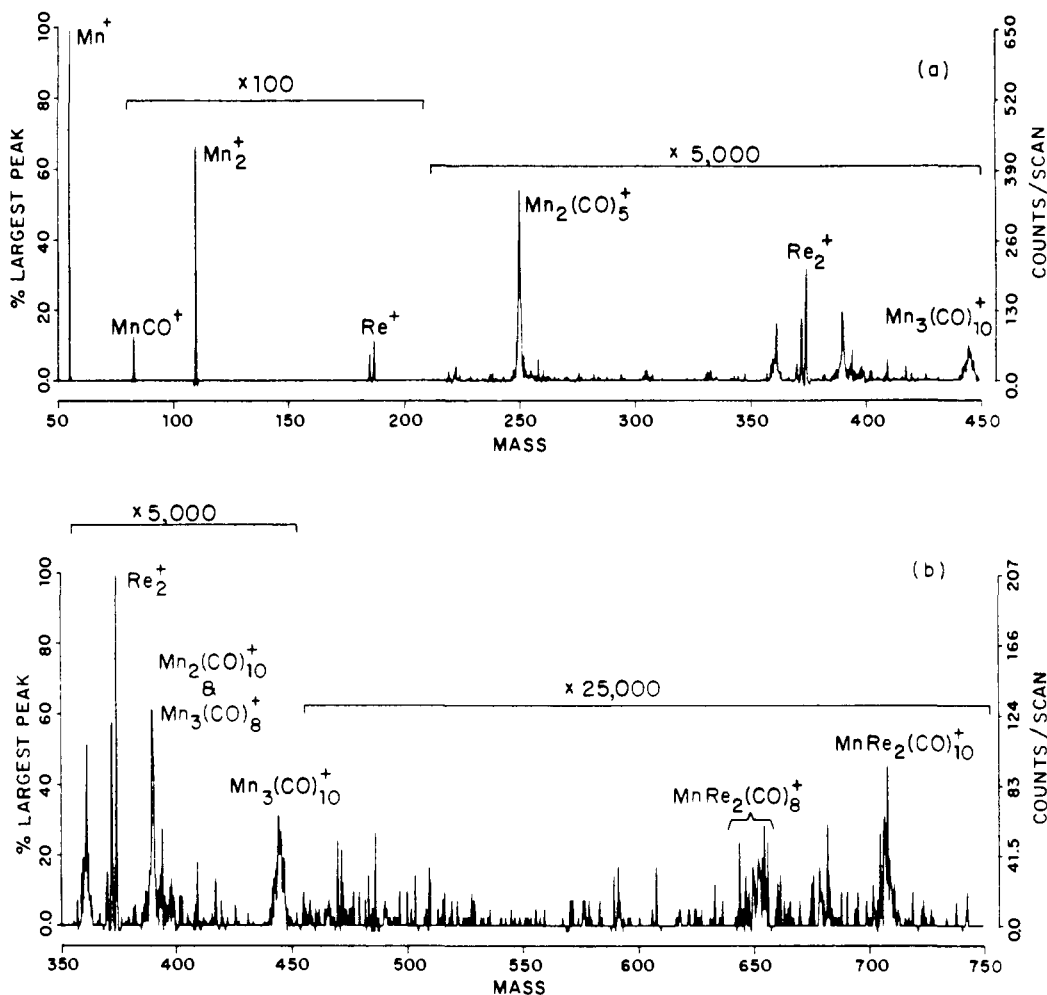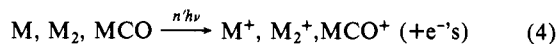

Figure 4. MPI mass spectrum form 1:10 mixture of $Re_2(CO)_{10}$ plus $Mn_2(CO)_{10}$ (total pressure 3×10^{-5} torr), using 7.5-mJ laser pulses at 511.1 nm. Broad peaks, at masses >460, are due to the reaction of Mn^+ with $Re_2(CO)_{10}$. The Re_2^+ isotopic peaks at 370, 372, and 374 amu due to the direct MPI process, are sharp, demonstrating that the broadening of other peaks at high masses is not instrumental. Note that at the extreme amplification used in the high mass (reaction product) region of the spectrum, the smallest peaks are due to single ions.

(reactions 1 and 2), the fragments seen at low mass in the REMPI spectrum can be explained to occur as the result of initial photodissociation of the parent

$$M_2(CO)_{10} \xrightarrow{nh\nu} M, M_2, \text{ and } MCO \qquad (3)$$
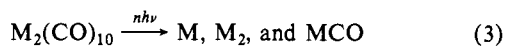
followed by ionization of these species

$$M, M_2, MCO \xrightarrow{n'h\nu} M^+, M_2^+, MCO^+ (+e^-\text{'s}) \qquad (4)$$
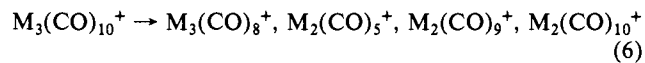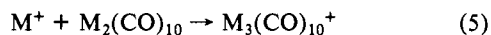
The nature of the neutral photoproducts observed points to the

chemically interesting fact that gas-phase photodissociation of $M_2(CO)_{10}$ proceeds by ligand dissociation both with and without cleavage of the M–M bond.[22]

While the low mass ions in the REMPI spectrum can be adequately explained by the above mechanism (reactions 3 and 4), the ions seen at high mass need further consideration. The peak widths in the REMPI TOF spectra of $M_2(CO)_{10}$ are large for $M_2(CO)_n^+$ and $M_3(CO)_m^+$ and narrow for the low (M^+, M_2^+, MCO^+) mass ions. The latter are characterized by sharp peaks comparable to those from the EI mass spectra. However, the high

mass peaks are significantly broader. Figure 4, for example, contains a direct comparison of the peak widths for the Re_2^+ isotopic triplet and $Mn_2(CO)_9^+$ at masses 370, 372, 374, and 362, respectively. As noted in the Results section, the intensities of the M^+, M_2^+, and MCO^+ peaks are linear with pressure while all $M_2(CO)_n^+$ and $M_3(CO)_m^+$ ions display a quadratic dependence. Of particular note is the occurrence of the addut or "superparent" $M_3(CO)_{10}^+$ peaks at high mass.

The results outlined above lead to the conclusion that the high mass fragments observed are a result of an efficient recombination process. The ion–molecule reaction below is the most likely path to the high mass ions.

$$M^+ + M_2(CO)_{10} \rightarrow M_3(CO)_{10}^+ \qquad (5)$$

$$M_3(CO)_{10}^+ \rightarrow M_3(CO)_8^+, \ M_2(CO)_5^+, \ M_2(CO)_9^+, \ M_2(CO)_{10}^+ \qquad (6)$$

The rate-limiting step in this reaction is formation of the M^+ ion, as indicated by the wavelength dependence of the signal (at fixed mass) which is enhanced when the laser is tuned to an atomic resonance. The efficiency of such ion–molecule reactions is high.

While ion–molecule reactions involving transition-metal ions have been studied by ICR techniques,[16] there are few reports on reaction of metal ions with transition-metal carbonyls. The reaction products of $Mn^+ + Mn_2(CO)_{10}$ investigated in a recent ICR experiment[17] consist of $Mn_2(CO)_n^+$, $n = 5$, 7–9. On the longer

timescale (ms) of the ICR experiment $Mn_3(CO)_{10}^+$ is not observed. The estimated lifetime of this unstable ion is therefore on the order of microseconds. The remarkable stability of such an energetic species can be understood in terms of the large numbers of modes available to support the excess (recombination) energy. Bond dissociation energies for $M_3(CO)_{10}^+$ are not available; however, in general, M–M bond cleavage and CO dissociation are both expected fragmentation processes for $M_3(CO)_{10}^+$. The process $M_3(CO)_{10}^+ \rightarrow Mn(CO)_5 + Mn_2(CO)_5^+$ responsible for the efficient formation of the product $Mn_2(CO)_5^+$ is not unexpected since loss of $Mn(CO)_5$ is the most common process in the photodissociation[8,9] of $Mn_2(CO)_{10}$. The small extent of fragmentation of $M_3(CO)_{10}^+$ is consistent with a limited excess energy in $M_3(CO)_{10}^+$, as verified by crude RRK calculations.

In the field of ion–molecule reactions, similar complexes of comparable lifetimes have previously been reported for several reactions, e.g., $RX^+ + RX$ (X = I etc.),[18] $C_6H_5^+ + C_6H_6$,[19] $C_2N_2^+ + C_2N_2$,[20] and others involving polyatomic organic ions.[21] The present study is believed to be the first report of such "adduct complexes" involving transition-metal carbonyl compounds.

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Secondary Ion Mass Spectrometry of Small-Molecule Solids at Cryogenic Temperatures. 3.[1] Nitrogen Oxides

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Abstract: Secondary ion mass spectra of neat solids N_2O, NO, N_2O_3, and N_2O_4 were measured as a function of the nature and energy of the primary ions (He^+, Ne^+, Ar^+, Kr^+, Xe^+, 0.5–4.5 keV). All of the solids produced a rich variety of positive and negative secondary ions. Particularly striking is the abundance of cluster ions, observed above all for primary ions of large momentum. The elemental composition of the "elementary solvating units" generally does not agree with the molecular formula of the solid, suggesting that extensive ion–neutral and neutral–neutral chemistry occurs before the cluster ion reaches the mass analyzer. A qualitative model for these processes is proposed.

The use of secondary ion mass spectrometry to extend the capability of mass spectrometry to new types of substrates has developed rapidly in recent years.[2] It is hardly surprising that it has generated considerable interest in many areas of potential application such as obtaining mass spectra of involatile compounds[2–4] and of matrix isolated species.[5,6] The method involves

the bombardment of a solid surface by a beam of primary ions which causes the ejection of neutral particles and both positive and negative ions from the solid. The secondary ions are mass analyzed by a mass spectrometer, resulting in secondary ion mass spectra (SIMS).

Relatively little is known with certainty about the fundamental processes which are involved in the formation of secondary ions and their subsequent emission. In this respect, it appears that the investigation of solids composed of very simple molecules with simple fragmentation patterns might be helpful. A few such

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