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Laser Ablation-Molecular Beam Method: A Versatile Diagnosis for the Reactions of Metal Ions with Molecules in the Gas Phase. Dimanganese Decacarbonyl(1)

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Intense laser light was focussed on the surface of a metal substrate (Nb or Cu) in vacuum, and a molecular beam of $Mn_2(CO)_{10}$ was injected nearby. Product ions resulting from the reaction of substrate metal ions or electrons with $Mn_2(CO)_{10}$ were analyzed by mass-spectroscopy. This method provides a simple and versatile diagnosis for the reactions of metal ions and/or electrons with molecules in the gas phase.

The ion-molecular reactions of metal ions with organic or organometallic molecules in the gas phase have extended a rich field of organometallic chemistry.(2-7) The laser ionization method in combination with ion cyclotron resonance and Fourier transform mass spectroscopy(3-7) has been used to obtain the organometallic ions. However, many sophisticated instruments, which are also highly expensive, have been used in these studies. In this letter we propose a much simpler method to study these reactions, combining laser ablation of a metal substrate in vacuum and injection of a molecular beam nearby. A preliminary result on the case of a Nb or a Cu metal substrate with the beam of $Mn_2(CO)_{10}$ is given.

The schematic view of the experimental setup is shown in Fig. 1. A mass spectrometer system composed of a quadrupole mass spectrometer (Extrel, 4-162-8, inner diameter 9.5 mm) and a detector (Ceratron from Murata) was set in a vacuum chamber. The back pressure without the molecular beam was ca. 10^{-6} Torr. A Nb or a Cu metal substrate, electrically grounded, was located at

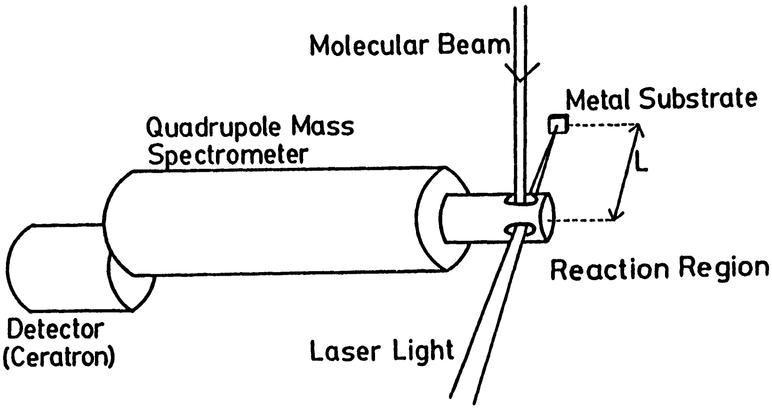

Fig. 1. Schematic view of experimental setup.

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the distance of 4 cm from the entrance region of the ion lens assembly of the mass filter. The 2nd harmonics (532 nm) of a Quanta-Ray DCR-2 Nd:YAG laser was focussed on the surface of this metal substrate. This caused ejection of substrate metal ions along with photoelectrons. A pulsed molecular beam of $Mn_2(CO)_{10}$ was supplied into the entrance region through a modified automobile fuel injector which was externally driven electrically. The substrate metal ions and electrons flowed into the entrance region and reacted with $Mn_2(CO)_{10}$ molecules. The entrance region is hereafter called reaction region, and so marked in Fig. 1. Product ions given as the result of ion- and electron-molecular reaction were detected by the mass spectrometer system.

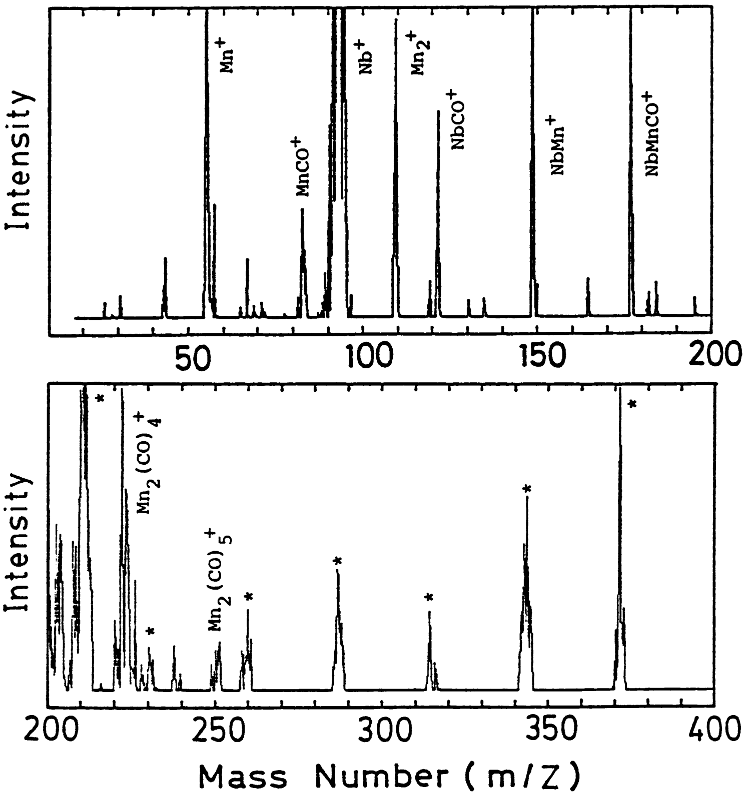

Fig. 2. Mass spectrum obtained on laser irradiation focussed on an Nb substrate with a molecular beam of $Mn_2(CO)_{10}$ injected nearby. (See Text.)

In the absence of the molecular beam, only the singly charged substrate metal ion (Nb^+ or Cu^+) was detected. Neither cluster ions nor doubly charged ions were found. The typical mass spectrum obtained for a Nb substrate with the molecular beam of $Mn_2(CO)_{10}$ is given in Fig. 2. Besides the substrate metal ion, Nb^+ (m/z = 93), and fragment ions resulting from the metal carbonyl, i.e., $Mn_2(CO)_5^+$ (250), $Mn_2(CO)_4^+$ (222), Mn_2^+ (110), $MnCO^+$ (83), and Mn^+ (55), many types of ions were detected. Among them $NbCO^+$ (121), $NbMn^+$ (148), and $NbMnCO^+$ (176) were found. The other signals with asterisks can be attributed to $NbMn_2(CO)_n^+$, n = 0 - 6 (m/z = 203, 231, 259, 287, 315, 343, and 371), and/or $NbMn(CO)_n^+$, n = 2 - 8 (m/z = 204, 232, 260, 288, 316, 344, and 372).

Concerning the ions originating from $Mn_2(CO)_{10}$, it is known that the photolysis of $Mn_2(CO)_{10}$ in near-UV region gives either $Mn(CO)_5$ or $Mn_2(CO)_9$ as the product depending on the excitation wavelength, and that the shorter wavelength favors the latter species.8) Ridge et al.9) found Mn^+, $Mn(CO)_n^+$ (n = 1 - 3, 5, 6), Mn_2^+ and $Mn_2(CO)_n^+$ (n = 1 - 5, 10) on the electron impact of $Mn_2(CO)_{10}$ at 70 eV. Among them the abundant species were Mn^+, Mn_2^+, and $Mn_2(CO)_n^+$ (n = 4, 5). In our case no parent ion $Mn_2(CO)_{10}^+$ was found, and those four species which were abundant in the experiment of Ridge et al. were observed. These fragment ions are due to the reaction of $Mn_2(CO)_{10}$ with electrons from the substrate, as shown below for $Mn_2(CO)_5^+$. On the other hand, those ions which contain Nb and Mn are apparently given by the ion-molecular reaction $Nb^+ + Mn_2(CO)_{10}$. Figure 3 shows the time after laser pulse when three types of ions, (a) $Mn_2(CO)_5^+$ (m/z = 250), (b) Nb^+ (93), (c) $NbMn(CO)_4^+$ (260), were detected. The transit time in the quadrupole, which is larger for higher m/z value, is not subtracted. It is obvious that $Mn_2(CO)_5^+$, a fragment ion from $Mn_2(CO)_{10}$, was formed in the reaction region well before Nb^+ arrived there. Therefore, $Mn_2(CO)_5^+$ must have been formed by the reaction, not with the Nb^+ ion, but with a much fast-flying species. Photoelectron is the only candidate. $NbMn(CO)_4^+$ is obviously given by the reaction with Nb^+, and the difference in the time of detection of these two ions, ca. 13 μs (measured at the peak), reflects partly the difference in their transit times in the quadrupole. The difference may partly be due to the different velocity distribution of total Nb^+ ions and those which can cause the reaction with $Mn_2(CO)_{10}$.

Figure 4 shows the mass spectrum obtained for a Cu substrate and the molecular beam of $Mn_2(CO)_{10}$. Again,

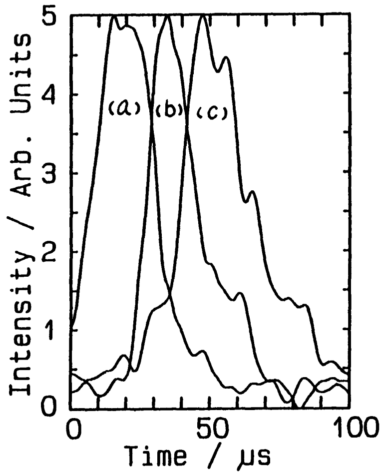

Fig. 3. Time distributions for detection of cations after the laser pulse. (a) $Mn_2(CO)_5^+$ (m/z = 250), (b) Nb^+ (93), (c) $NbMn(CO)_4^+$ (260). The transit time in the quadrupole is not subtracted. The intensities are normallized at the peak.

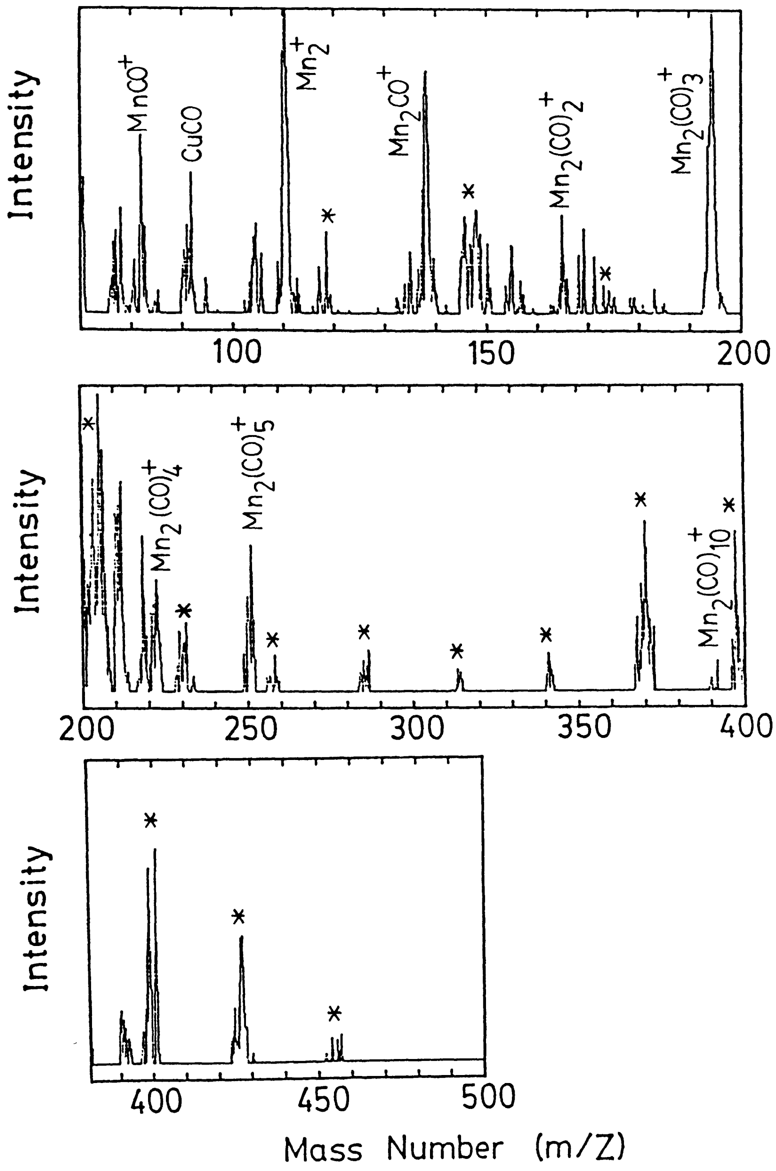

Fig. 4. Mass spectrum obtained on laser irradiation focussed on a Cu substrate with a molecular beam of $Mn_2(CO)_{10}$ injected nearby.

besides the substrate metal ion, Cu^+ (m/z = 63, not shown), and ions resulting from $Mn_2(CO)_{10}$, i.e., $Mn_2(CO)_n{}^+$ (n = 0 - 5, 10) and $MnCO^+$ (83), many types of complex ions due to ion-molecular reaction appeared. They are $CuCO^+$ (91) and those with asterisks in the figure, i.e., $CuMn_2(CO)_n{}^+$, n = 0 - 10 (m/z = 173, 201, 229, 257, 285, 313, 341, 369, 397, 426 and 454) and/or $CuMn(CO)_n{}^+$, n= 0 - 10 (m/z = 118, 146, 174, 202, 230, 258, 286, 314, 342, 370, and 398). Some of the peaks are due to unidentified origin. It is noteworthy that a complete set up to the species without any loss of CO moiety has been found in this case.

Formation of mixed metal carbonyls by laser irradiation on a metal substrate in the presence of metal carbonyl vapor has been reported by Kappes and Staley$^{6)}$ for $Cr(CO)_6$ or $Ni(CO)_4$ with a variety of metal cations using the ion cyclotron resonance instrument. Our method is much simpler, and much less expensive than theirs. It can nonetheless unravel many important features in the reaction of metal cations with many types of organic or organometallic substances. Toya et al.$^{10)}$ used the simple apparatus reported here, and irradiated a variety of metal substrates with a laser and introduced the molecular beam of tetramethyltin near-by. They obtained only fragment ions of tetramethyltin by the reaction with photoelectrons. In their system laser light was less tightly focussed than the present experiment. In the present system both processes of ion- and electron-molecular reactions are found, and we can compare the reactivity of metal ions and electrons obtained on laser irradiation of a metal substrate.

Further studies on such ion-molecular reactions are under way. We believe that such a method provides a simple and versatile diagnosis for the study of ion- and/or electron-molecular reactions between the metal ion and organic or organometallic compounds.

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