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LIF detection of molybdenum atoms in the collisionless 5 μ m infrared multiphoton decomposition of Mo(CO)₆

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Abstract

The observation of Mo atom production by collisionless infrared multiphoton decomposition (IR MPD) of Mo(CO)₆ with second harmonic radiation ($\approx 5 \ \mu$ m) of a TEA CO₂ laser is reported. Mo atoms in the ground state a ⁷S₃ have been detected by the UV laser induced fluorescence technique. The production of naked metal atoms has been explained by a sequence of IR MPD processes of parent Mo(CO)₆ molecules and vibrationally excited photofragments Mo(CO)_x (x < 6).

1. Introduction

The photochemistry of organometallics has been actively studied with UV and visible lasers for more than 15 years (see, for example, Ref. [1]). Early investigations showed that the UV multiphoton decomposition (MPD) of metal carbonyls and other organometallics efficiently produces neutral metal atoms in their ground and excited electronic states [2,3]. Two mechanisms, sequential and concerted ones, were proposed for the UV MPD of metal carbonyls. The former proceeds through successive discrete one-photon absorption and fragmentation steps, and the latter through the direct absorption of two or more UV photons before fragmentation, followed by the 'explosive' decomposition of a parent molecule to a metal atom and carbon monoxide molecules [4].

In contrast to the numerous photochemical studies of metal carbonyls, the infrared laser chemistry of these compounds has received less attention because it was difficult to obtain a suitable excitation source. The indirect excitation and decomposition of metal carbonyls through collisions with excited SF₆ molecules were studied using an intense CO₂ laser, and the properties of the product materials have been reported [5-8]. Metal carbonyls have strong infrared absorption bands close to 2000 cm⁻¹ due to CO stretching vibrations. Simple frequency doubling of ¹²CO₂ laser lines does not give infrared radiation at the centers of these bands. Therefore, the infrared multiphoton decomposition (IR MPD) of transition metal carbonyls $M(CO)_6$ (M = Cr, Mo and W) has thus far been studied using the doubling of $^{13}CO_2$ laser lines and the sum frequency generation of two synchronized ${}^{12}CO_2$ lasers as excitation sources [9–11]. In these experiments facile IR MPD of M(CO)₆ was observed even at laser fluences lower than 0.1 J cm⁻² with laser lines in the region of 2000 ± 5 cm^{-1} , which covers the strong absorption bands of

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 $M(^{12}CO)_6$, and only ultrafine metal particles and CO molecules were found as final products. Similar results were obtained in the IR MPD of Fe(CO)₅ with *p*-H₂ Raman shifted radiation of a CO₂ TEA laser [12], which coincides with the Fe–CO bending vibration of Fe(CO)₅ at 620 cm⁻¹. However, the detailed process of decarbonylation has not been explained and the mechanism of metal particle formation has not been understood to date. Moreover, bare metal atoms in the IR MPD of metal carbonyls have never been detected.

In this Letter it is shown that the collisionless IR MPD of refractory transition metal carbonyls such as $Mo(CO)_6$ results in the formation of naked metal atoms, which have been detected by the time-resolved laser induced fluorescence (LIF) technique. The formation of bare metal atoms most likely proceeds through the IR MPD of parent Mo(CO)₆ molecules and sequential secondary photolysis of vibrationally excited unsaturated metal carbonyl species Mo(CO)_x (x < 6).

2. Experimental

The time-resolved LIF technique combined with a pulsed 5 µm laser was used for the detection of decomposition products in the 5 µm IR MPD of Mo(CO)₆. A CO₂ TEA laser (Lumonics, TEA-820), operated at a repetition rate of 1 Hz, was tuned to the R(30) line of the $00^{0}1-10^{0}0$ transition at 982.10 cm^{-1} , which was doubled by a nonlinear crystal of AgGaSe₂ with a size of $14 \times 14 \times 20$ mm³ (NPO 'Ametist', Krasnodar, Russia). Typical output and pulse duration of the frequency doubled 5 µm laser (at 1964.2 cm⁻¹) were 30 mJ per pulse and 60 ns fwhm, respectively. This laser line is 40 cm⁻¹ lower than the CO stretching band of $Mo(^{12}CO)_6$ but only 6 cm^{-1} lower than the ¹³CO stretching band of the $Mo(^{12}CO)_{s}(^{13}CO)$ species (natural abundance of 6.78%) [13]. Therefore, it can be expected to cause the IR MPD of the latter species with the present excitation source. Chemiluminescence has been observed when mixtures of $M(CO)_6$ (M = Cr, Mo and W) and O_2 molecules were irradiated with a 5 μ m laser at the same frequency as used here, which was explained by the IR MPD of the M(¹²CO)₅(¹³CO) species and reactions of the resulting unsaturated transition metal carbonyls with oxygen [14]. In the

present experiments the 5 μ m laser beam was focused into the center of a reaction cell with a BaF₂ lens (focal length 20 cm). The diameter of the laser beam was about 1 mm at the focal point. The laser fluence was changed by inserting plastic films in front of the BaF₂ lens, so as not to change the position and size of the focused beam.

Ground-state (a^7S_3) Mo atoms produced in the IR MPD were excited at 313.26 nm (y ${}^{7}P_{4}^{o} \leftarrow a^{7}S_{3}$ transition [15]) using a Nd:YAG laser pumped dye laser system (Continuum, ND6000) with an autotracker (Inrad, AutotrackerII), and fluorescence from the excited state $(y^{7}P_{4}^{o})$ was detected at the same wavelength. The UV laser beam with a diameter of ≈ 0.5 mm was set orthogonally to the IR laser beam to monitor only the central part of the focal region of the IR beam, and the fluence of the UV laser was attenuated to 10 μ J cm⁻² with neutral density filters to avoid any UV multiphoton processes in the parent molecules and products. An LIF signal was observed at right angles to both laser beams with a photomultiplier tube (PMT, Hamamatsu, R928), in front of which a monochromator (Jasco, CT10) was placed. The time evolution of the Mo atoms was obtained by changing the delay time between the IR and UV laser pulses. The IR laser pulse transmitted through the cell was monitored with a photon-drag detector (PDD, Hamamatsu, B749) and a pyroelectric detector (Molectron, 20D). The UV laser signal was monitored with a PIN photodiode sensor (PDS) and used as a trigger signal for a digital oscilloscope (Tektronix, TDS420), in which the signals from the PMT, PDS and PDD were averaged and stored. The averaged records in the oscilloscope were transferred to a personal computer and analyzed. The glass reaction cell was equipped with two CaF₂ windows for the IR laser beam, two quartz windows for the UV probe laser beam and a quartz lens (focal length 6 cm) for detection of the LIF signal.

A solid sample of $Mo(CO)_6$ (Strem, 99%) was placed into a glass reservoir connected with the reaction cell. The sample was degassed by several freeze-pump-thaw cycles with liquid N₂ prior to use and then maintained at 273 K with an ice bath. The vapor of $Mo(CO)_6$ at 273 K passed slowly through the cell and its pressure was measured with an absolute pressure gauge (MKS, 220BH) attached to the cell.

3. Results

All experiments in this study were performed at pressures as low as 1 mTorr to avoid any influence of collisions. Under this low pressure condition, the gas-kinetic collision time is about 100 μ s, which is two orders of magnitude longer than the time region studied here. Fig. 1A shows the typical time evolution of the 5 μ m IR laser (curve 1), UV laser (curve 2) and the LIF signal of Mo atoms (curve 3) obtained in a single-shot experiment. Because the lifetime of the excited state y ⁷P_4^o of Mo atoms (5.6 ns [15]) is shorter than the pulse duration of the UV probe (10 ns fwhm), the shape of the LIF signal is close to that of the probe light. It is seen that Mo atoms already appear at ≈ 50 ns after the onset of the IR pulse. The modulation of the IR pulse is due



Fig. 1. (A) Real-time evolution of the 5 μ m IR laser pulse at 1964.2 cm⁻¹ (curve 1), the UV probe pulse at 313.26 nm (curve 2) and the LIF signal of Mo atoms ($y^7 P_4^0 - a^7 S_3$ transition) at the same wavelength (curve 3). (B) LIF intensity (circles) as a function of the delay time between maxima of the IR and UV laser pulses, obtained from the IR MPD of 1 mTorr Mo(CO)₆ at a laser fluence of 3 J cm⁻². Each data point is the average of 80 shots. The dashed curve represents the averaged intensity profile of the IR laser.



Fig. 2. LIF intensity of the Mo atom transition ($y^7 P_4^0 - a^7 S_3$) as a function of IR laser fluence, obtained at a delay time of 2 µs from 1 mTorr Mo(CO)₆. Each data point is the average of 80 shots. At laser fluences less than 0.8 J cm⁻² an LIF signal could not be observed. A representative error bar ($\pm 20\%$) is shown for one of the points.

to partial mode locking of the CO₂ laser. The shift $(\approx 30 \text{ ns})$ between the UV probe and the LIF signal is due to instrumental delay between the PMT and PDS responses. Such single-shot signals were averaged for 80 shots and then normalized to the UV laser intensity to obtain LIF intensities with an experimental error of less than 20%. The averaged LIF intensities of Mo atoms, measured at an IR fluence of $\approx 3 \text{ J cm}^{-2}$, are shown in Fig. 1B as a function of the delay time between the IR and UV pulses. The dashed curve represents an averaged profile of the 5 μ m IR laser, which is a little broadened due to the jitter $(\pm 25 \text{ ns})$ of the CO₂ laser. The LIF signal increases rapidly to about 60% of the maximum intensity during the IR pulse. Even after the pulse is completed, the increase in the LIF signal continues to around 1 µs and then saturates. Afterwards the LIF signal decays with an apparent lifetime of ≈ 8 μ s due to the motion of atoms out of the zone probed by the UV laser (not shown in the figure). The relative amount of atoms produced during the IR laser pulse depends on the IR laser fluence. At a fluence of $\approx 1 \text{ J cm}^{-2}$ only 10% of the totally produced Mo atoms are formed during the laser pulse.

Fig. 2 shows LIF intensities observed at a delay time of 2 μ s as a function of IR laser fluence *F*, which is plotted on a log-log scale. The yield of Mo atoms increases about 300 times over the fluence range 0.8-3.3 J cm⁻². In the fluence region around 1 J cm⁻² the LIF intensity can be expressed by a function $F^{5.5}$ and in the region around 3 J cm⁻² by a function $F^{3.2}$, which are shown by dashed lines in Fig. 2. This steep relationship indicates no saturation of the Mo atom production even at the maximum fluence examined here. At laser fluences lower than 0.8 J cm⁻² the formation of ground state a⁷S₃ Mo atoms was not observed, which was due to the detection limit of the present experimental apparatus.

4. Discussion

The results presented above unambiguously demonstrate that a molybdenum hexacarbonyl molecule loses all carbonyl ligands and produces a Mo atom on irradiation with an intense 5 µm laser under collision-free conditions. Here we will discuss which mechanism, the concerted or the sequential one described in the introduction, is probable for the formation of the Mo atom in the IR MPD of Mo(CO)₆. The energies necessary to remove the first and all carbonyl ligands were reported to be 170 and 910 kJ mol⁻¹, respectively [5]. Therefore, to produce a Mo atom from Mo(CO)₆, at least 39 infrared photons (1 photon $\approx 23.5 \text{ kJ} \text{ mol}^{-1}$) should be absorbed and more than 31 photons in the dissociation continuum, which is the energy region above the first dissociation limit. Considerable vibrational excitation above the dissociation limit is known for large polyatomic molecules (see, for example, Ref. [16]). In the dissociation continuum, the vibrational excitation of Mo(CO)₆ competes with the unimolecular dissociation of the parent molecule to CO and $Mo(CO)_5$. The rate of dissociation increases rapidly with increased energy above the dissociation limit. At the energy corresponding to the formation of a Mo atom and six CO molecules, the rate can be estimated to be larger than the order of 10^{12} s⁻¹ using RRKM theory [17]. In the concerted mechanism, where a Mo atom and six CO molecules are produced from Mo(CO)₆ in one step, the vibrational excitation should be faster than the unimolecular dissociation with the rate mentioned above.

The linear excitation rate is given by $\sigma_0 F/h\nu\tau$, where σ_0 , F, $h\nu$ and τ are the linear absorption cross section, laser fluence, photon energy and duration of the laser pulse, respectively. From the infrared spectra of gaseous Mo(CO)₆ with natural isotopic composition σ_0 is obtained as 1.5×10^{-17} cm^2 at the laser position of 1964 cm^{-1} , which is mainly due to the $Mo({}^{12}CO)_{5}{}^{13}CO$ species. Under the present experimental conditions, $F \approx 0.8-3.3$ J cm⁻² and $\tau \approx 60$ ns (fwhm), the excitation rate is estimated as $(1-4) \times 10^{10}$ s⁻¹. Because this value is much lower than that required for the concerted mechanism, the formation of Mo atoms in the 5 µm IR MPD of $Mo(CO)_6$ is probably due to the sequential mechanism, where vibrationally excited $Mo(CO)_{6}$ decomposes to a CO molecule and vibrationally excited Mo(CO)_s species, which further absorbs infrared radiation and dissociates to smaller species in the pulse duration under collision-free conditions, that is.

$$Mo(CO)_{5}({}^{13}CO) \xrightarrow{nh\nu} Mo(CO)_{5}^{*} \xrightarrow{nh\nu} Mo(CO)_{4}^{*}$$
$$\xrightarrow{nh\nu} Mo(CO)_{3}^{*} \xrightarrow{nh\nu} Mo(CO)_{2}^{*}$$
$$\xrightarrow{nh\nu} MoCO^{*} \xrightarrow{nh\nu} Mo, \qquad (1)$$

where the asterisk and n indicate the vibrationally excited species and the number of photons absorbed, respectively. All the unsaturated molybdenum carbonyl species Mo(CO), (x < 6) have strong absorption bands in the range 1900-2000 cm⁻¹ due to CO stretching modes [18]. Because these species are produced in various vibrational states, their absorption bands should be much broader than those of ground vibrational states. Therefore, the 5 µm photons can be strongly absorbed by the $Mo(CO)_r^*$ species without close resonance of the laser line to the absorption bands of cold Mo(CO), species. Similar long pathways are known for the IR MPD of polyatomic molecules with a CO₂ laser, for example, the formation of C_2 in the 10 μ m IR MPD of C₂H₃CN is thought to proceed through the following sequence [19]:

$$C_{2}H_{3}CN \xrightarrow{hh\nu} C_{2}H_{2}CN \xrightarrow{hh\nu} C_{2}HCN \xrightarrow{} \xrightarrow{hh\nu} C_{2}CN \xrightarrow{} \xrightarrow{hh\nu} C_{2} + CN.$$
(2)

The above simple equation (1) qualitatively explains the formation of Mo atoms during the IR laser pulse. The increase in LIF intensity after the laser pulse, shown in Fig. 1B, is considered to be due to unimolecular dissociation of MoCO^{*} with a small amount of excess energy above the dissociation limit. The rate of Mo atom formation after the laser pulse can be estimated as 2.5×10^6 s⁻¹ from Fig. 1B, which may correspond to the average rate of the unimolecular dissociation.

No tendency of saturation for the Mo atom formation has been found in the fluence range studied (see Fig. 2), suggesting the existence of rate determining steps in Eq. (1). We could not obtain enough information to specify them definitely. However, another experimental result, in which the relative fraction of Mo atoms produced during the laser pulse depends on infrared laser fluence, implies that the excess energy of MoCO* changes with the fluence, and therefore at least the last step of Eq. (1) is not saturated under the present experimental conditions. This may be supported by the fact that the MoCO species is expected to be strongly bounded (bond dissociation energy 150 ± 60 kJ mol⁻¹ [17]) and that the facile IR MPD of such a triatomic molecule is generally difficult without close coincidence between the laser line and the absorption band.

When the CO stretching mode of $Mo(^{12}CO)_6$ was excited at 2003 cm⁻¹, complete decomposition of Mo(CO)₆ accompanied by metal particle formation was observed even at laser fluences as low as 50 mJ cm⁻² in previous experiments [9,11]. Our results have demonstrated Mo atom formation in the collisionless IR MPD of Mu(¹²CO)₅¹³CO, but no saturation has been observed even at relatively high fluences such as 3 J cm⁻². One reason for this large discrepancy is that the absorption cross section of $Mo({}^{12}CO)_6$ at 2003 cm⁻¹ is about eight times larger than that of $Mo({}^{12}CO)_5{}^{13}CO$ at 1964 cm⁻¹. Another possibility is that in the previous experiments the final yield of decomposition was measured and therefore secondary processes such as bimolecular reactions between Mo(CO), could play a large role in the total decarbonylation [9].

5. Conclusions

The IR MPD of $Mo(CO)_6$ has been studied under collision-free conditions using an IR laser at 1964.2

cm⁻¹ and the LIF technique. At IR laser fluences larger than 0.8 J cm^{-2} , the formation of ground-state Mo atoms has been observed in the duration of the IR pulse and also after the pulse, which can be qualitatively explained by a sequential mechanism. shown as Eq. (1). In addition to the results reported here, we have also observed the LIF signal of Cr atoms in the 5 μ m IR MPD of Cr(CO)₆ [20]. The generation of metal atoms seems to be a general feature of the IR MPD of metal carbonyls. The present technique for the production of metal atoms can be considered as complementary to laser or electron beam ablation of bulk metals and also to the UV MPD of metal complexes. This study shows directly that intense infrared laser irradiation can remove all ligands from a molecule consisting of a central atom and surrounding ligands, through vibrational excitation under collision-free conditions.

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