

FORMATION AND LUMINESCENCE OF MOLYBDENUM ATOMS AFTER UV MULTIPHOTON EXCITATION OF GAS PHASE $\text{Mo}(\text{CO})_6$

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The delayed luminescence of Mo atoms was observed in XeCl laser excitation of $\text{Mo}(\text{CO})_6$ gas. The observed luminescence was explained by production of Mo Rydberg atoms under UV laser excitation of $\text{Mo}(\text{CO})_6$.

KEY WORDS: Metal carbonyls, Rydberg atoms, UV multiphoton excitation.

1. INTRODUCTION

Photodissociation of metal carbonyls in gas phase under UV radiation has been extensively studied for a long time. In one of the first papers on this subject it was shown that $\text{Fe}(\text{CO})_5$ molecule can lose its CO ligands under UV excitation.¹ The investigation of UV multiphoton dissociation (MPD) of organometallic molecules shows that MPD of practically any of such molecules yields mainly metal atoms or ions.² For example, the excitation of gas-phase $\text{Mo}(\text{CO})_6$ by UV laser radiation ($\lambda = 193 \text{ nm}$, 248 nm , 351 nm) with a low fluence (about several mJ/cm^2) gives mainly $\text{Mo}(\text{CO})_5$, $\text{Mo}(\text{CO})_4$, $\text{Mo}(\text{CO})_3$.^{3,4} As the laser fluence increases, radicals with a smaller number of CO ligands and Mo atoms begin to appear among the photodissociation products. At higher fluences (hundreds of mJ/cm^2) Mo^+ ions are formed.⁵ The formation of Mo atoms in different states under the KrF laser excitation of the $\text{Mo}(\text{CO})_6$ ($\lambda = 248 \text{ nm}$) with a moderate fluence (5 to $40 \text{ mJ}/\text{cm}^2$) was observed in Reference 6. The population distribution of the atoms over the excited states in the energy range from 25000 to 35000 cm^{-1} was found to be Boltzmann with a characteristic temperature of $11000 \pm 2500 \text{ K}$.

The luminescence of Mo atoms from different energy levels was observed after excitation of gas-phase $\text{Mo}(\text{CO})_6$ by XeCl laser radiation ($\Phi = 100 \text{ mJ}/\text{cm}^2$).⁷ The interesting feature of this luminescence is appearance of the delayed atomic emission, along with the well known luminescence which occurs simultaneously with the laser pulse. The time delay between the laser pulse and the maximum of the delayed luminescence pulse is about a few hundreds of nanoseconds. We found several transitions from highly excited atomic levels which result in delayed Mo emission after XeCl laser excitation of $\text{Mo}(\text{CO})_6$.

In this paper we present our study of the delayed atomic emission which appeared at the $z^7P^0 \leftarrow e^7D$ transition of Mo under XeCl laser excitation of $\text{Mo}(\text{CO})_6$ gas.

2. EXPERIMENTAL

The experimental setup comprised a XeCl-laser ($\lambda = 308$ nm, pulse width $\tau = 15$ ns (FWHM), energy $E = 50$ mJ), a stainless-steel vacuum chamber ($120 \times 350 \times 350$ mm) having quartz windows ($\varnothing 60$ mm), a monochromator (slit spectral width $20 \text{ \AA}/\text{mm}$) and a gated optical multichannel analyzer (OMA). The spectral resolution was 2 \AA . The temporal evolution of luminescence at a certain fixed wavelength was studied using a photomultiplier (spectral response 200 to 800 nm). The laser radiation was focused into the chamber with a quartz lens ($f = 20$ cm), the laser fluence in the observation region was about $300 \text{ mJ}/\text{cm}^2$. The luminescence signal was accumulated with its subsequent averaging, by using the digital oscilloscope and a computer.

The vacuum chamber was evacuated to 10^{-5} Torr with an oil-diffusion pump fitted with a liquid-nitrogen trap. The $\text{Mo}(\text{CO})_6$ pressure range used was 0.02 to 0.1 Torr. The pressure of the buffer gas was varied between 0.01 and 500 Torr.

The $\text{Mo}(\text{CO})_6$ carbonyl was commercial-grade and was sublimed and stored under vacuum before being used.

3. RESULTS

A large number of atomic Mo lines are observed in the luminescence spectrum when $\text{Mo}(\text{CO})_6$ is excited by XeCl-laser with the fluence $\Phi = 300 \text{ mJ}/\text{cm}^2$. The luminescence of Mo_2 dimers is also presented in the spectrum.

Delayed atomic lines present a special interest. These are atomic lines of Mo whose intensity reaches a maximum in several hundreds of nanoseconds after a laser pulse and then slowly, in several microseconds, decreases (Figure 1). Delayed luminescence was studied for the $z^7P_4^0 \leftarrow e^7D_{3-5}$ transitions, the most intense line corresponds to the transition $z^7P_4^0 \leftarrow e^7D_5$. This transition is started at an energy of 44970.10 cm^{-1} and is terminated at 26320.38 cm^{-1} . The radiative time for these transitions is only of the order of ten nanoseconds. It should be noted that there was not any distinct luminescence from levels close to the e^7D_j level.

The tail of the luminescence pulse (Figure 1) shows a near exponential decay. The decrease of the tail emission intensity can be characterized by a single decay time, τ_D . This is the time interval when the tail intensity drops from 1 to $1/e$. To characterize the whole pulse of the delayed atomic emission we also used time integrated luminescence intensity, I_{int} .

Figure 2 shows the dependences of τ_D and I_{int} on the pressure of $\text{Mo}(\text{CO})_6$. The characteristic time, τ_D , practically does not depend on $\text{Mo}(\text{CO})_6$ pressure in the range 0.02 to 0.1 Torr. The pressure dependence of I_{int} shows the slope 1.8 ± 0.5 .

Figures 3a,b present the influence of different buffer gases on delayed luminescence.

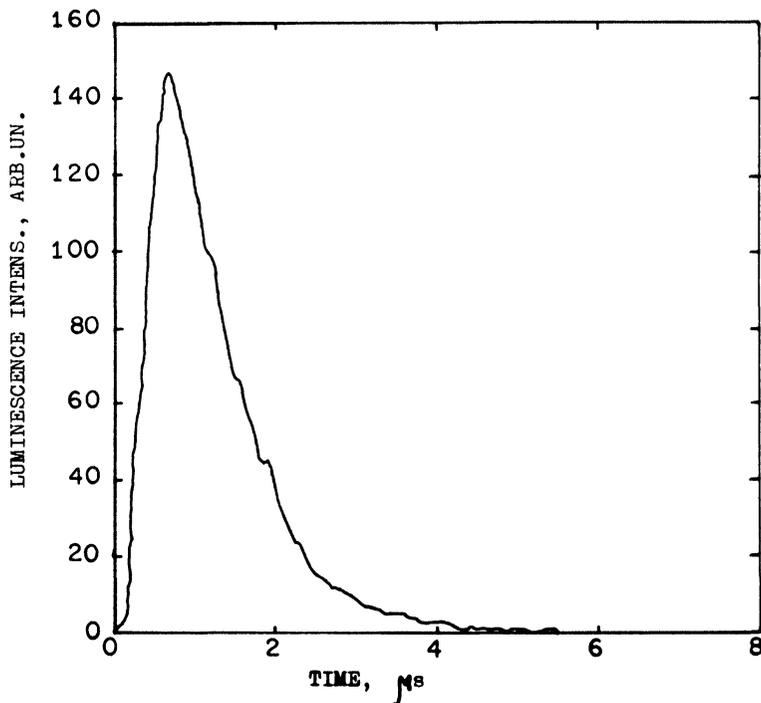


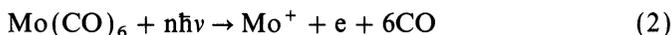
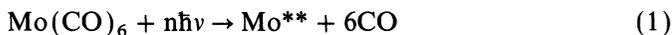
Figure 1 Kinetics of delayed Mo luminescence at the transition $z^7P_4 \leftarrow e^7D_5$ ($\lambda = 534.06$ nm), $\text{Mo}(\text{CO})_6$ pressure is 0.04 Torr.

The time-integrated intensity, I_{int} , and the luminescence decay time, τ_D , were measured as a function of buffer gas pressure. It has been found that with addition of noble gases (He, Ne, Ar, Kr, Xe) I_{int} increases and then drops almost to zero due to collisional relaxation. The decay time, τ_D , behaves in a similar way. The buffer gas pressure corresponding to maximum of I_{int} and τ_D decreases with atomic mass of the buffer gas. The only exception is Ne since the maximum of I_{int} and τ_D for this buffer is reached at higher pressures, about 100 Torr.

We studied also the influence of the electronegative gases CCl_4 and SF_6 on the delayed luminescence. Figure 4 shows the dependence of I_{int} on their pressure. The integral luminescence drops rapidly with the pressure of SF_6 and CCl_4 , starting with very low pressures: $2 \cdot 10^{-3}$ Torr for CCl_4 and $3 \cdot 10^{-2}$ Torr for SF_6 (Figure 4). The pressure of $\text{Mo}(\text{CO})_6$ in this case was 0.04 Torr.

4. DISCUSSION

Our experimental results can be explained by the production of Rydberg atoms in the UV excitation of $\text{Mo}(\text{CO})_6$. The most probable mechanism is as follows.



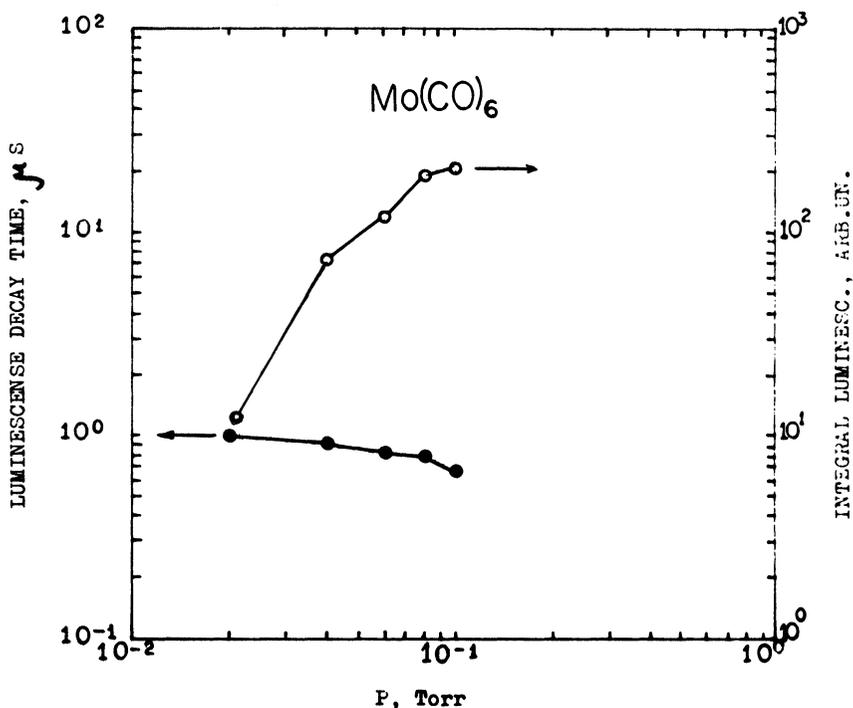
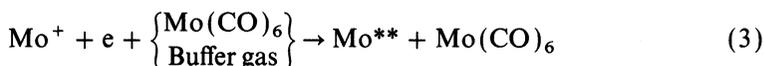


Figure 2 I_{int} and τ_D versus $\text{Mo}(\text{CO})_6$ pressure ($\lambda = 534.06 \text{ nm}$).



There are two possibilities of producing Rydberg atoms. The Mo atom created by UV excitation of $\text{Mo}(\text{CO})_6$ can be excited directly to Rydberg states by the same laser pulse (1). The UV laser excitation of $\text{Mo}(\text{CO})_6$ can create ions and relatively slow electrons (2), which are able to recombine when colliding with the parent molecule. The recombination process produces Rydberg atoms Mo^{**} (2).

The radiative decay of Rydberg atoms populates the e^7D_{3-5} atomic state and gives rise to delayed atomic emission at the transition $z^7P_4^0 \rightarrow e^7D_{3-5}$.

Finally, the laser radiation gives rise to highly excited Rydberg atoms in various states which can be divided into two groups: $A\ddagger^*$ are Rydberg atoms prepared in the states the direct radiative transitions from which to the e^7D_j state are forbidden and $A\ddagger^*$ are Rydberg atoms in the levels the transitions from which to the e^7D_j state are allowed and relatively fast (small principal quantum number n). Let us suppose that the fraction of $A\ddagger^*$ atoms is very low compared to $A\ddagger^*$. As a result of their collisions with the buffer gas or with parent molecules $\text{Mo}(\text{CO})_6$, the Rydberg atoms $A\ddagger^*$ transfer to $A\ddagger^*$. The transition to the Rydberg states, $A\ddagger^*$, may occur both due to relaxation with a change in the main quantum number n and due to the mixing

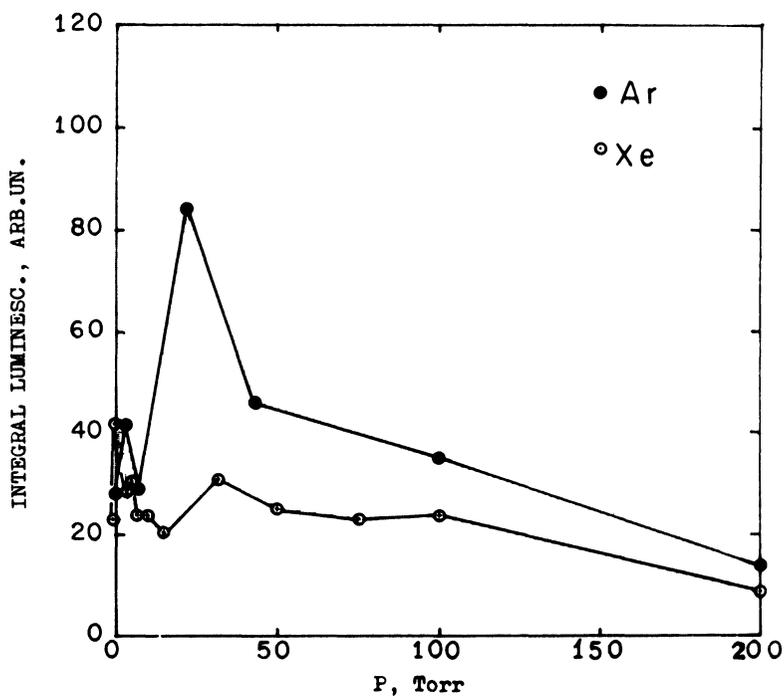
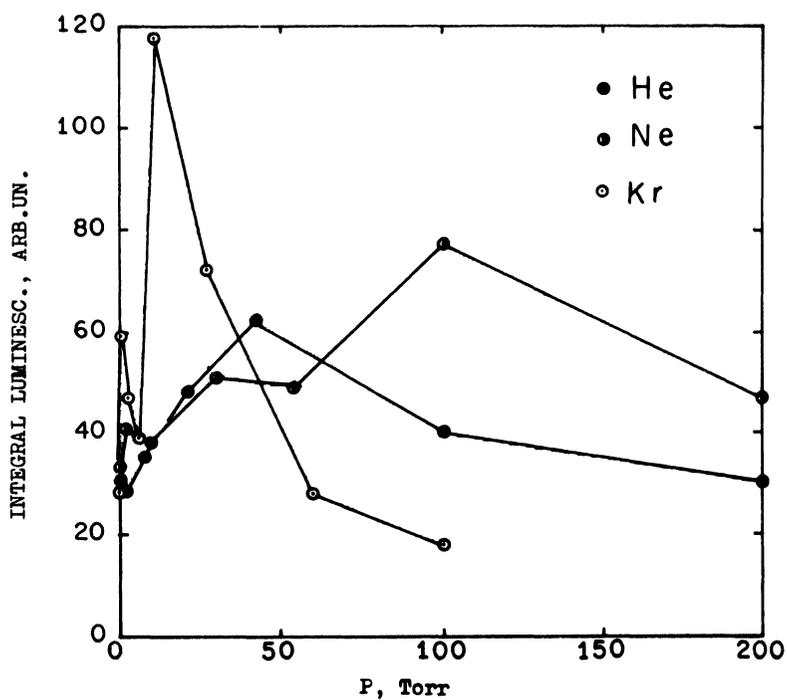


Figure 3 a, b. The dependence of I_{int} on buffer gas pressure ($\lambda = 534.06 \text{ nm}$): (a) He, Ne, Kr; (b) Ar, Xe. The pressure of $\text{Mo}(\text{CO})_6$ in both cases was 0.04 Torr.

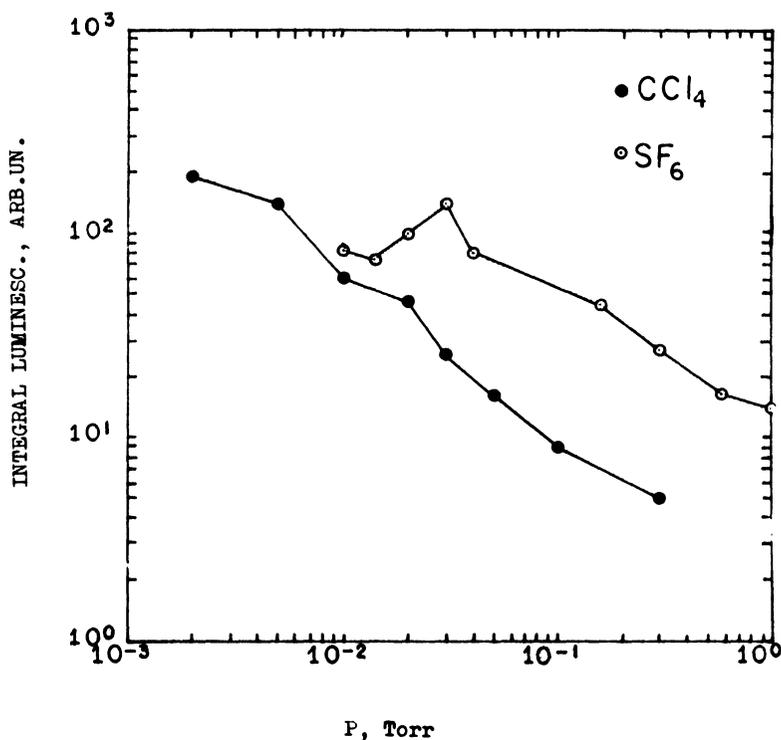


Figure 4 The dependence of I_{int} on CCl_4 and SF_6 pressures ($\text{Mo}(\text{CO})_6$ pressure was 0.04 Torr).

of states with different quantum numbers l and the same energies.⁸ Then $A_{\frac{1}{2}}^*$ decay to the e^7D_j state, and the radiative transition from this state to $z^7P_j^0$ is recorded as delayed luminescence. The subsequent transition to the ground state a^7S_3 from $z^7P_j^0$ can be also observed in the luminescence spectrum.

The dependence of integral luminescence intensity, I_{int} , on $\text{Mo}(\text{CO})_6$ pressure should be linear for direct production of Rydberg atoms (1) or quadratic for creation of these atoms in the recombination process (2). The experimental results give the slope 1.8 ± 0.5 . It means that recombination mechanism (2) produces Mo Rydberg atoms.

The radiative lifetime of the $e^7D \rightarrow z^7P$ transition is only several nanoseconds and is much shorter than the characteristic times of delayed luminescence. Therefore, the time evolution of delayed luminescence is defined by the population kinetics of the $A_{\frac{1}{2}}^*$ Rydberg states. The leading edge of the luminescence pulse is determined by the transitions of atoms to the $A_{\frac{1}{2}}^*$ states, and the trailing edge depends on the lifetime of these states. The Rydberg state lifetime can be estimated from Reference 9. The decay time $\tau_D = 1.5 \mu\text{s}$ corresponds to the lifetime of Rydberg atoms in the state with the principal quantum number n being equal to 11. As the $\text{Mo}(\text{CO})_6$ pressure rises or some buffer gas is added, the transitions from $A_{\frac{1}{2}}^*$ to $A_{\frac{1}{2}}^*$ states are accelerated

which makes the leading edge shorter. The initial increase of integral luminescence, as the buffer gas pressure rises, can be apparently explained by collisional transitions to A_2^{**} from other Rydberg states. A further increase in buffer gas pressure makes the collisional relaxation of A_2^{**} state faster which leads to luminescence quenching with higher buffer gas pressures.

An anomalously weak influence of Ne gas on delayed luminescence (Figure 3) can be explained also in the frame of the processes (1)–(3). It is well known that the Ne scattering length for thermal electrons is smaller than that for other noble gases.⁹ The scattering of thermal electrons is similar to those of Rydberg atoms since the electron in a Rydberg atom is far from the nucleus and hence is loosely bound to it.

The experiments with electronegative gases also confirm the Rydberg atoms hypothesis. When the SF_6 and CCl_4 molecules collide with a Rydberg atom, they trap the Rydberg electron and ionize the atom. The rapid decrease of integral luminescence with the pressure of electronegative gases points to the presence of such a process (Figure 4). The effect of CCl_4 on luminescence begins to manifest itself at partial pressures lower than in the case of SF_6 , which seems to be connected with a higher value of the electron affinity (2.12 eV for CCl_4 and 1.48 eV for SF_6).¹⁰

5. CONCLUSION

The delayed atomic luminescence which occurs after excitation of gas-phase $Mo(CO)_6$ by XeCl laser can be explained by the production of Mo Rydberg atoms. Laser radiation gives rise to Rydberg Mo atoms that via the relaxation process populate the starting e^7D_j states. The optical transition from these states is observed as delayed luminescence. The long luminescence tail is caused by relatively long lifetimes of Rydberg atoms.

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