Formation of Mo/W carbonyls by laser-ablation method

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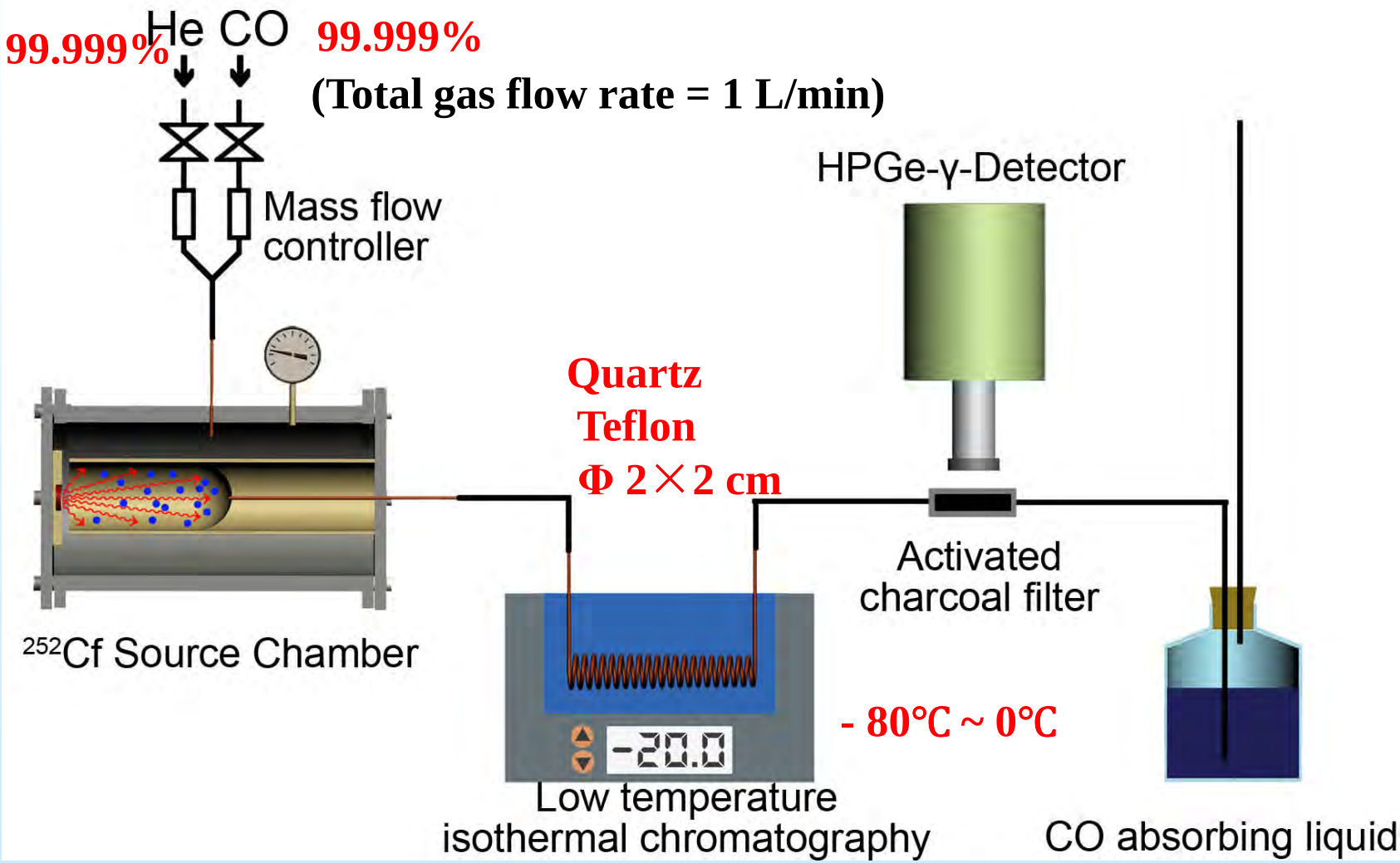
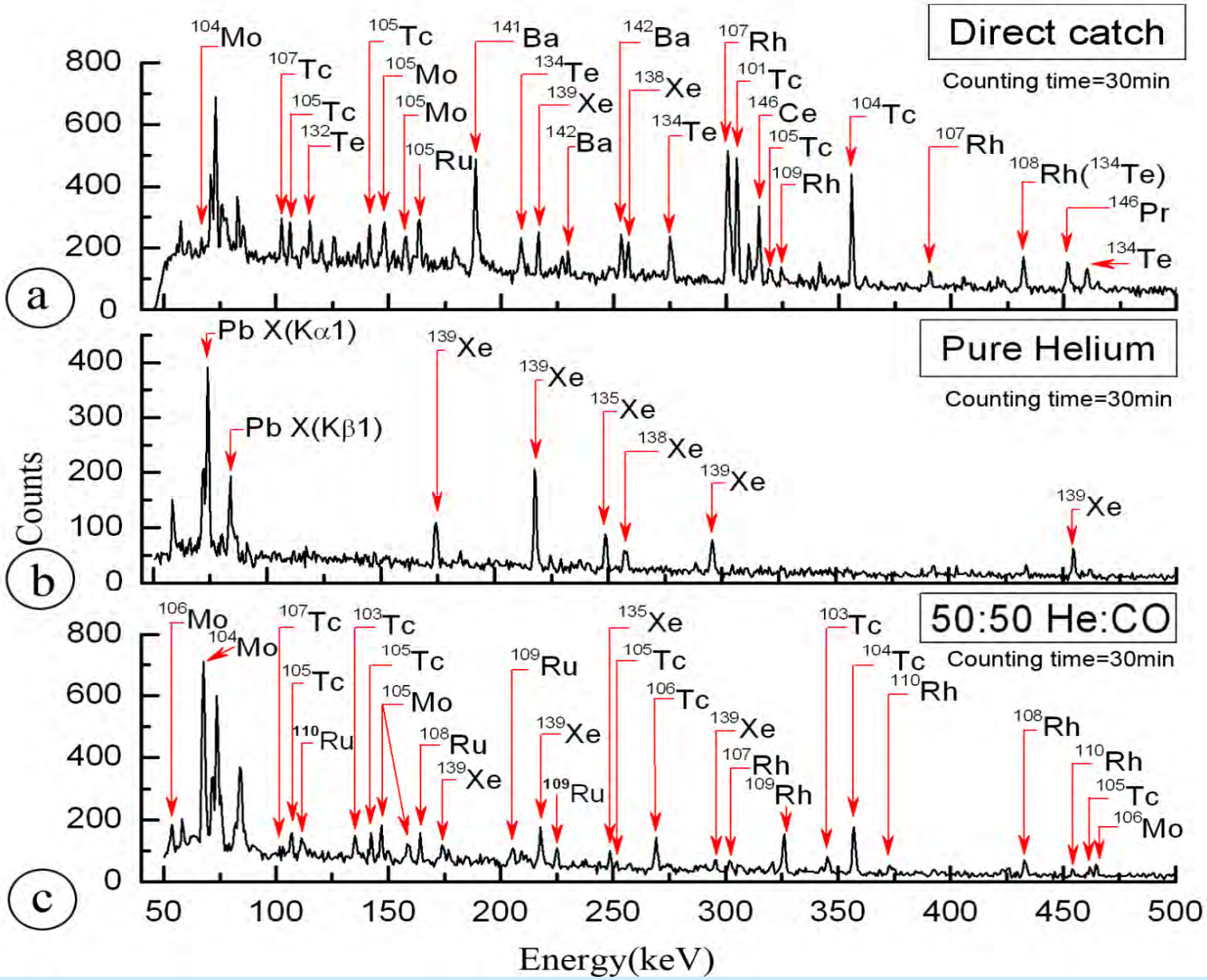
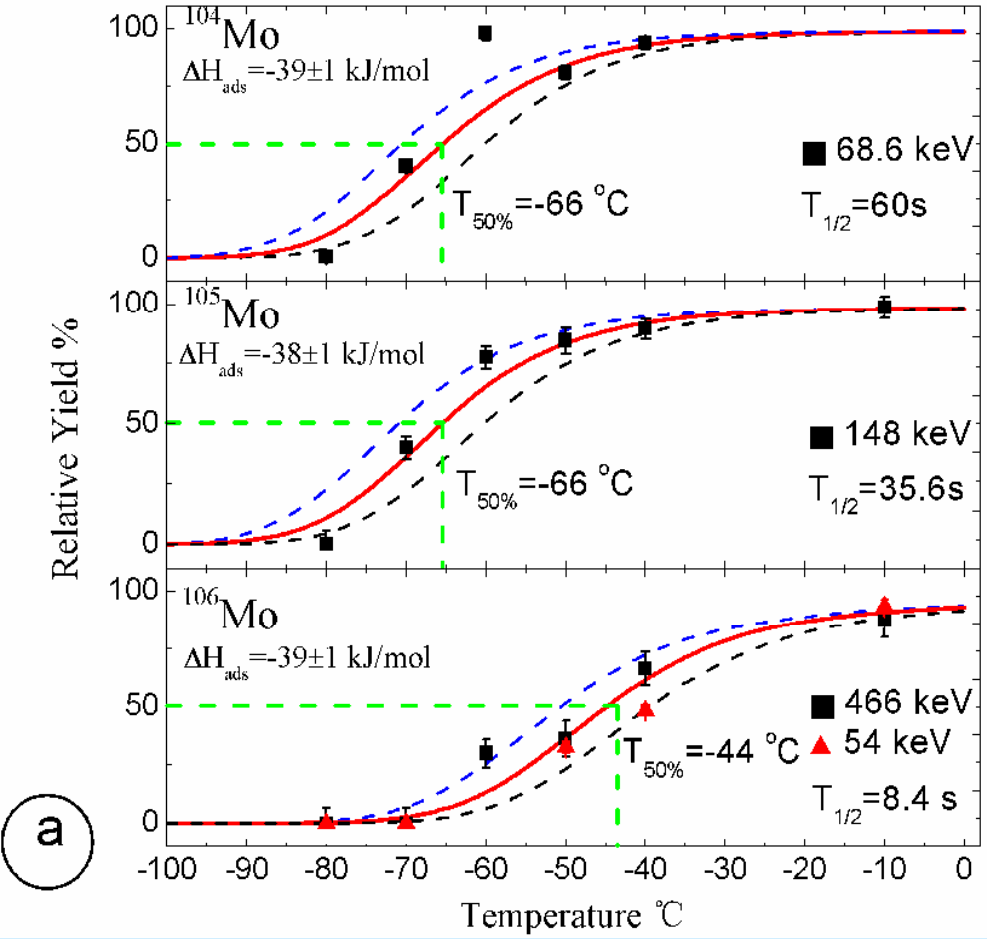
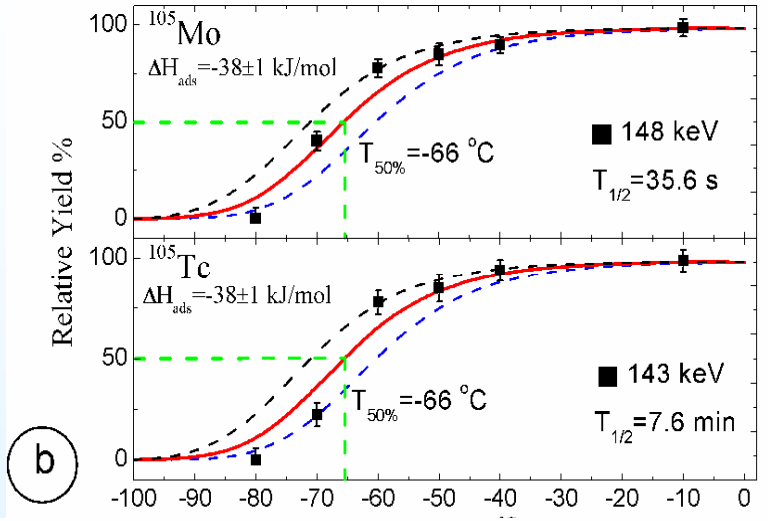
Gas-phase chemistry of Mo, Ru metal carbonyls

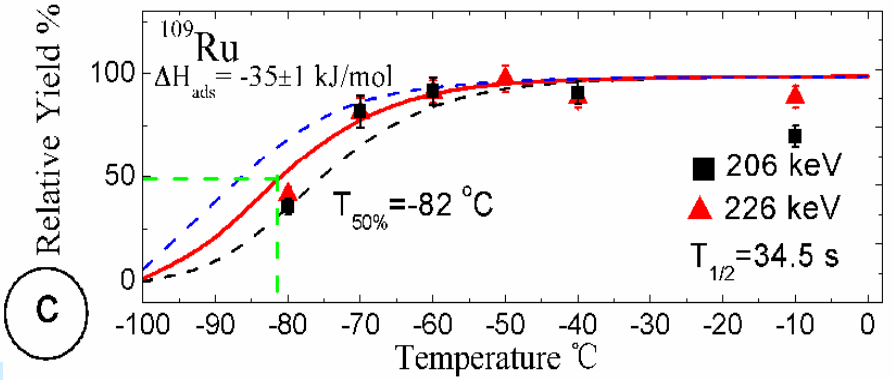
Radiochimca acta 102(2014)69-76,




Direct catch
Counting time=30min
Pure Helium
Counting time=30min
50:50 He:CO
Counting time=30min
a
b
c
Counts
Energy(keV)
104Mo
107Tc
105Tc
132Te
105Tc
105Mo
105Mo
105Ru
141Ba
134Te
139Xe
142Ba
142Ba
138Xe
134Te
107Rh
101Tc
146Ce
105Tc
109Rh
104Tc
107Rh
108Rh(134Te)
146Pr
134Te
Pb X(Kα1)
Pb X(Kβ1)
139Xe
139Xe
135Xe
138Xe
139Xe
139Xe
106Mo
104Mo
107Tc
105Tc
110Ru
103Tc
105Tc
105Mo
108Ru
139Xe
109Ru
139Xe
109Ru
135Xe
105Tc
106Tc
139Xe
107Rh
109Rh
103Tc
104Tc
110Rh
108Rh
110Rh
105Tc
106Mo

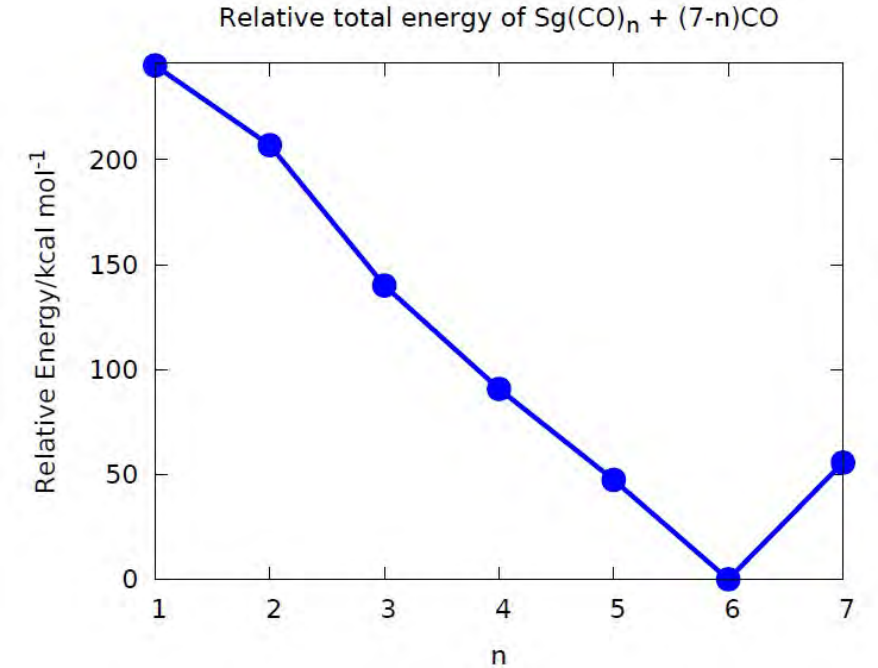






$T_{50\%}$ values for ^{105}Mo and ^{105}Tc are identical. ^{105}Tc was formed in the charcoal filter by β-decay of the transported precursor ^{105}Mo.

Theoretical calculation of the formation $Sg(CO)_n$ (n=1~7)



Sg + *x* CO → Sg(CO)*x* (x=1-7)

Jun Li, private communication

Conclusion

(1)This reaction is exothermic in thermodynamics and don not need potential barrier in dynamics.

(2)the generation of Sg(CO)*x* is *a* spontaneous cold atomic reaction.

(3)The stablity of Sg(CO)6 is the most high.

Question

(1) Is it a hot-atom chemistry?

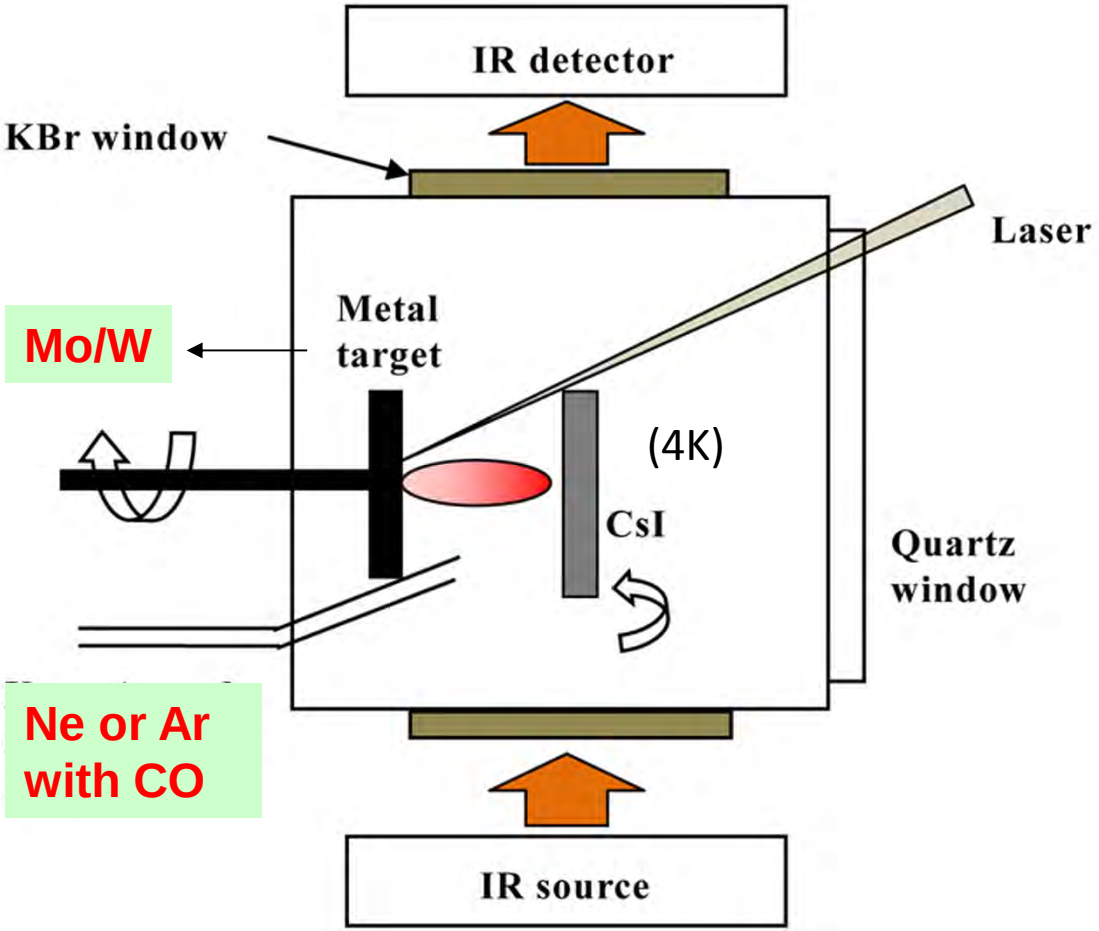
(2) Which kind of chemical compound is formed under our experiment condition?

Laser-ablation matrix-isolation @ infrared spectroscopy

***Mingfei Zhou*, Lester Andrews and Charles W. Bauschlicher, Jr.**
Spectroscopic and Theoretical Investigations of Vibrational Frequencies in Binary Unsaturated Transition-Metal Carbonyl Cations, Neutrals, and Anions
Chem. Rev. 2001, 101, 1931-1961

Prof. Mingfei Zhou, Department of Chemistry, Laser Chemistry Institute, Fudan University, Shanghai 200433, P. R. China

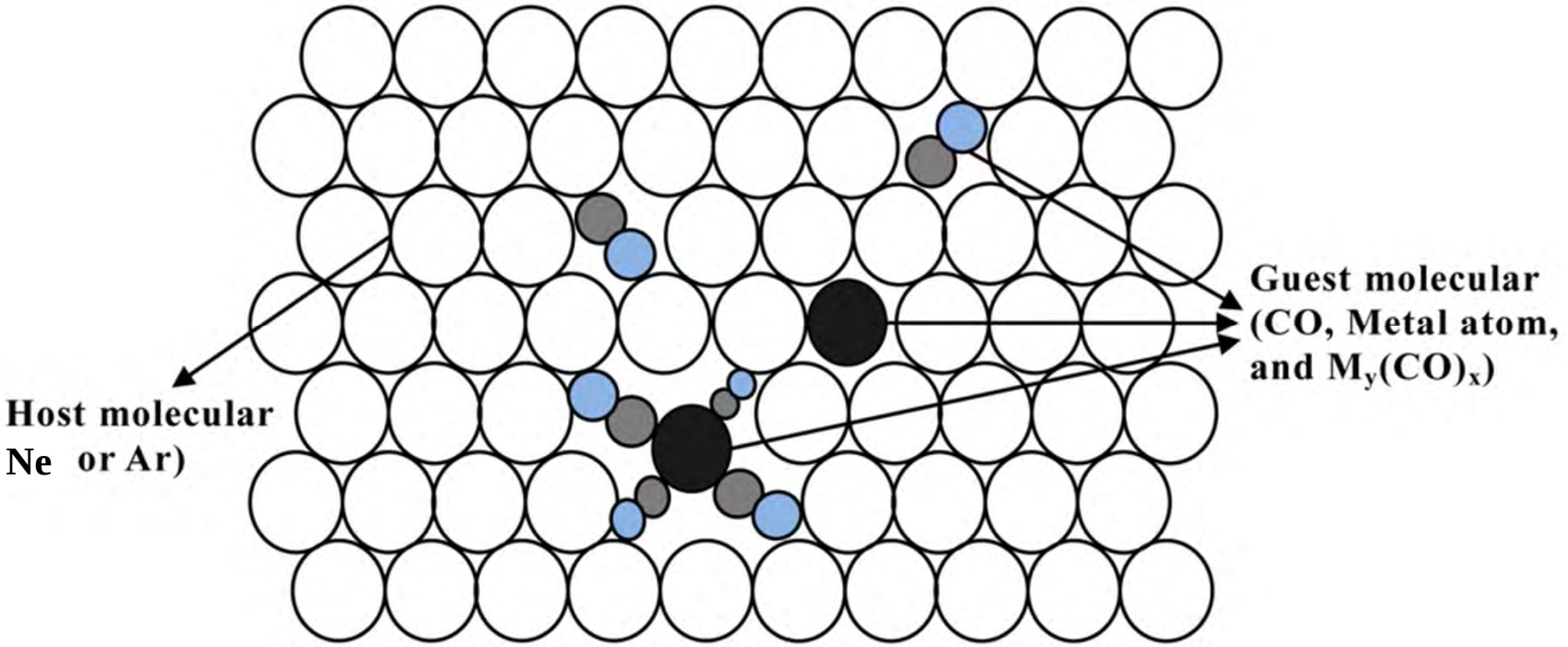
Experimental set-up at Fudan University



Laser irradiate rotating metal targets. Then laser-ablated metal atoms will be codeposited with CO (0.1-50%) in excess Ar onto a 4-5 K CsI cryogenic window for 30 min. And then Infrared spectra were recorded. The matrix samples will be annealed at different temperatures.

Laser-ablation matrix-isolation @ infrared spectroscopy

Schematic diagram of low temperature matrix-isolation technique



Comparison of gas phase Ne and Ar Matrix Frequencies (cm^{-1}) for Group 6 Carbonyls

	Mo			W		
	gas[a]	Ne[d]	Ar	gas[a]	Ne[d]	Ar
$M(CO)$		1881.2	1862.6[e]		1859.9	1848.8[e]
$M(CO)_2$		1895.2	1891.9[e]		1884.5	
$M(CO)_3$	1891	1886.1	1869[c]		1882.4	1865[c]
$M(CO)_4$	1972	1965.7	1951[c]	1957	1954.0	1939[c]
	1911	1908.9	1895[c]	1909	1909.0	1894[c]
$M(CO)_5$	1990	1984.5	1973[c]	1980	1975.9	1963[c]
	1942	1944.6	1933[c]	1942	1941.1	1932[c]
$M(CO)_6$	2003	2000.6	1992[c]	1998	1995.3	1986[c]
	598.6		587	588.5		

Lester Andrews, Mingfei Zhou, and Gennady L. Gutsev，, J. Phys. Chem. A,2003. 107:990-999

Reaction Mechanisms

Mo and W atoms react with CO on codeposition with excess neon and on annealing the solid to form all of the mononuclear carbonyls M(CO)***n*** (***n*** =1-6). Once formed, the MCO species readily add CO to produce the dicarbonyls, reaction 2.The yield of $M(CO)_3$ is small implying a slow reaction 3, but once formed, $M(CO)_3$ reacts rapidly with CO to form $M(CO)_{4,5,6}$. Because the saturated $M(CO)_6$ complexes have singlet ground states, fast reaction 4 suggests singlet states for the unsaturated $M(CO)_{3,4,5}$ intermediates.

$$Mo\ (^7S_3) + CO\ (^1\Sigma^+) \rightarrow MoCO\ (^5\Pi) \qquad (1a)$$

$$W\ (^5D_0) + CO\ (^1\Sigma^+) \rightarrow WCO\ (^5\Pi) \qquad (1b)$$

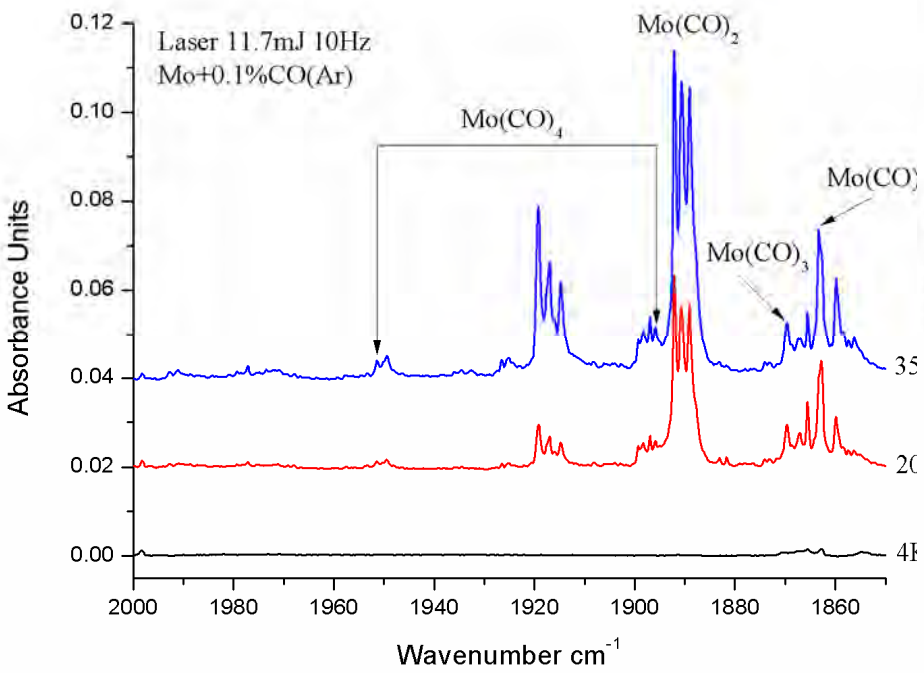
$$MCO\ (^5\Pi) + CO\ (^1\Sigma^+) \rightarrow M(CO)_2\ (^5A_2) \qquad (2)$$

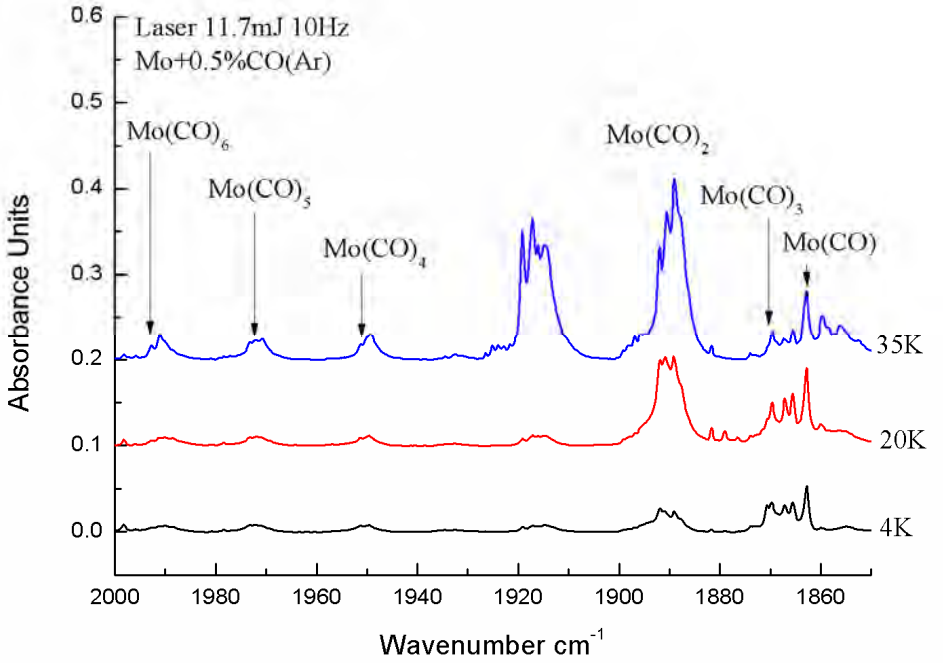
$$M(CO)_2\ (^5A_2) + CO\ (^1\Sigma^+) \rightarrow M(CO)_3\ (\text{singlet}) \qquad (3)$$

$$M(CO)_3\ (\text{singlet}) + 1,2,3CO\ (^1\Sigma^+) \rightarrow M(CO)_{4,5,6}\ (\text{singlet}) \qquad (4)$$

Lester Andrews, Mingfei Zhou, and Gennady L. Gutsev，, J. Phys. Chem. A,2003. 107:990-999

Experimental results



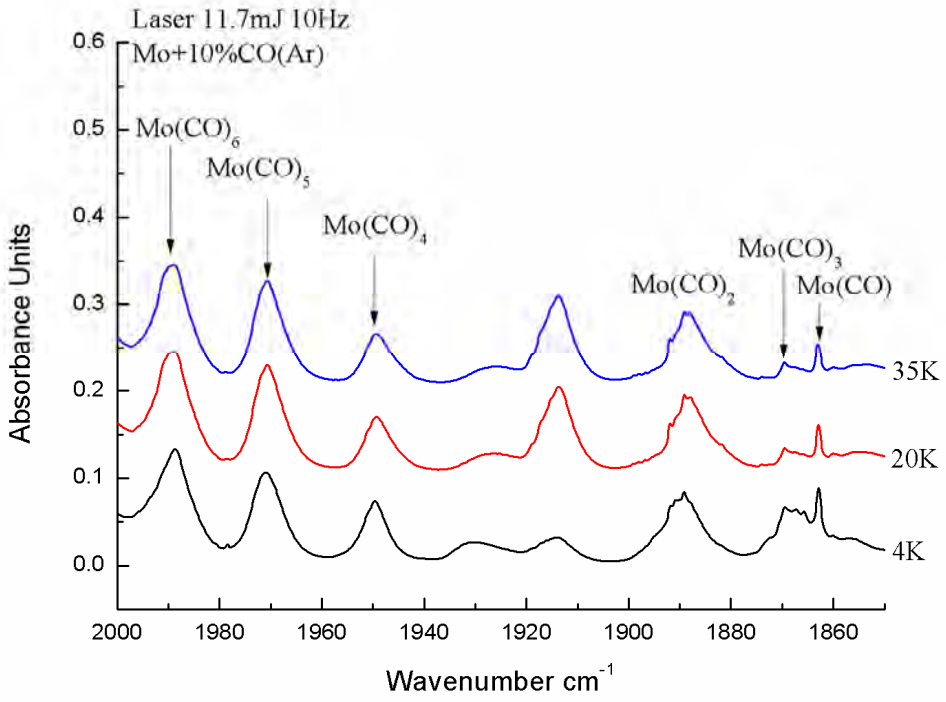


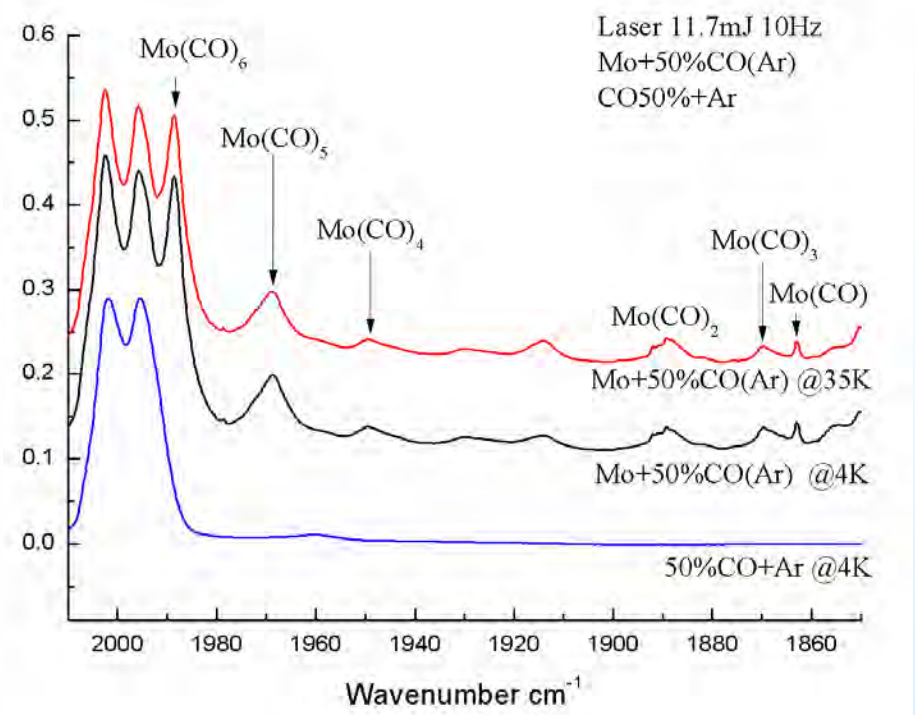
Infrared spectra of Mo-carbonyls as the function of temperature

For 0.1%CO in argon, no carbonyls was found at 4k. After annealing to 20 K, MoCO,$Mo(CO)_2$ and $Mo(CO)_4$ were observed. So this is not a “hot atom reaction ”

For 0.5%CO, MoCO and $Mo(CO)_2$ were found at 4k due to the more CO in the experiment. After annealing to 35 K, $Mo(CO)_6$ carbonyls appeared.

Experimental results



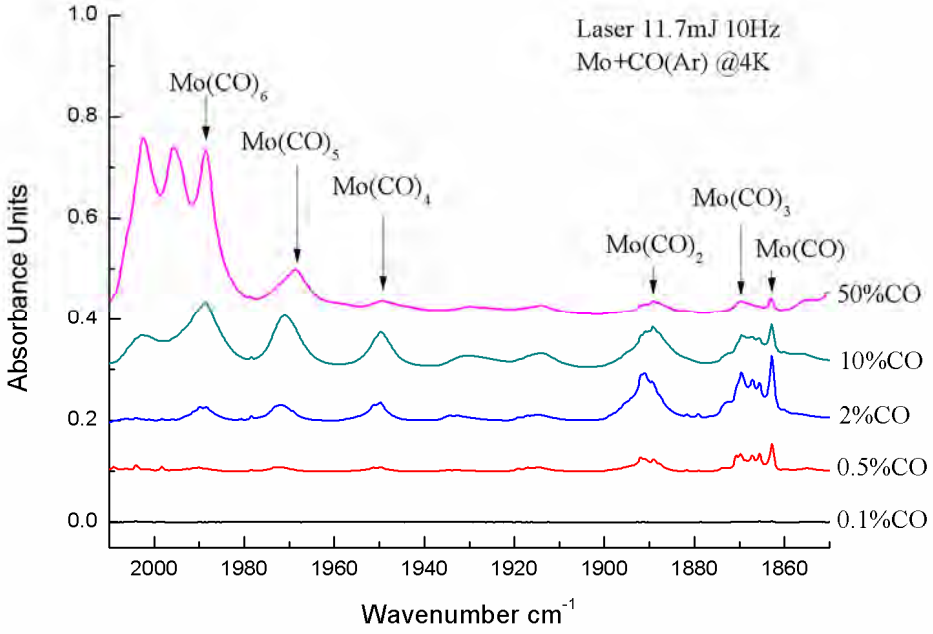


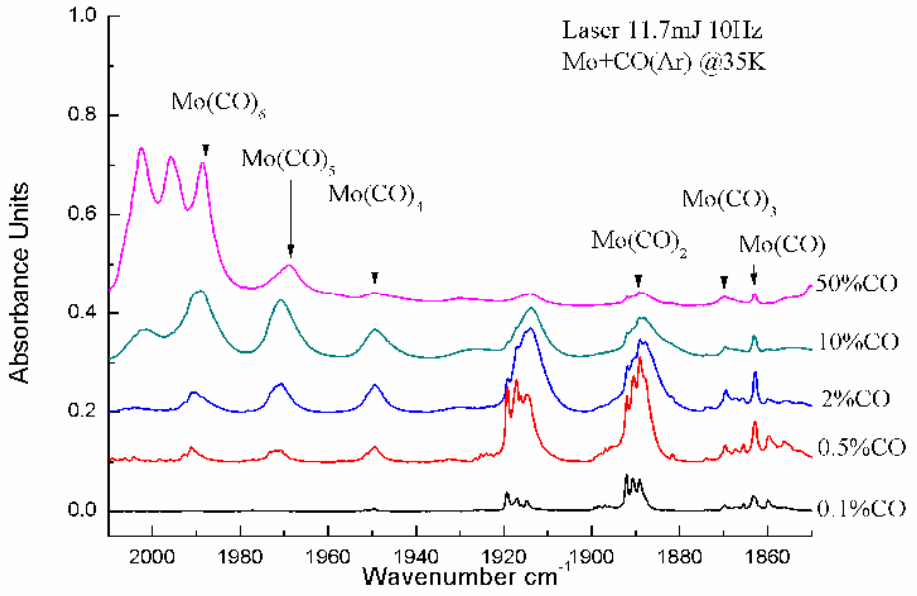
Infrared spectra of Mo-carbonyls as the function of temperature

When the concentration of CO was 10%, all of the mononuclear carbonyls M(CO)***n*** (***n***=1-6) were found at 4k.

For 50% CO, the saturated $Mo(CO)_6$ was the main products.

Experimental results

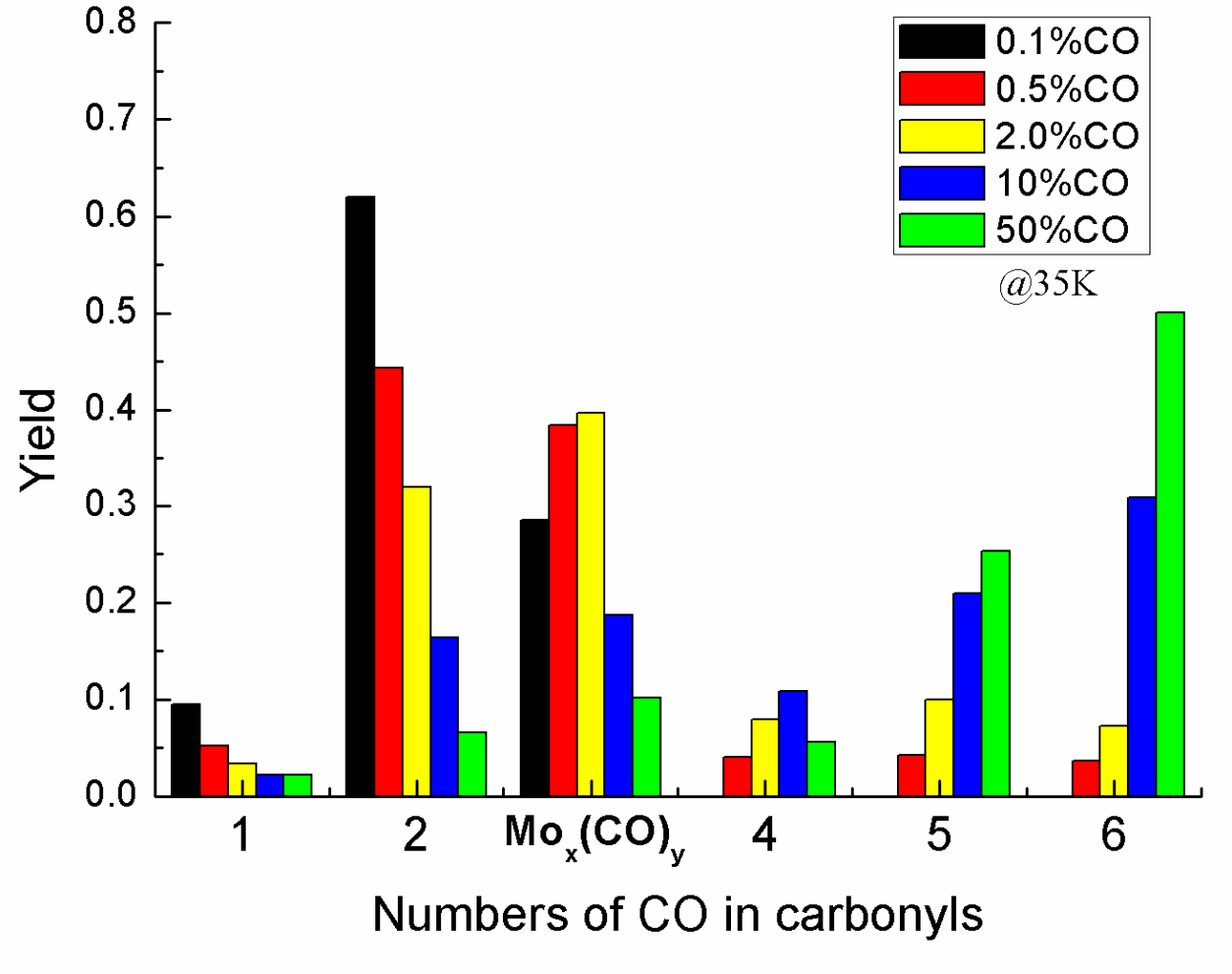




Infrared spectra of Mo-carbonyls for different concentration CO

With the increase of CO concentration under the same temperature, mononuclear carbonyls M(CO)***n*** (***n***=1-6) formed more easily and the saturated $Mo(CO)_6$ was the final stable products.

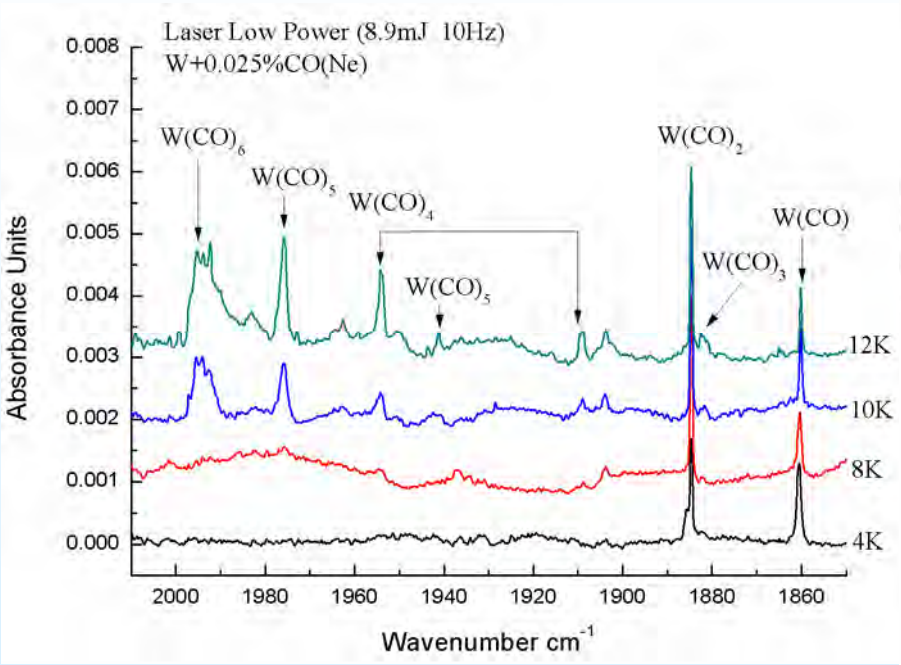
Experimental results

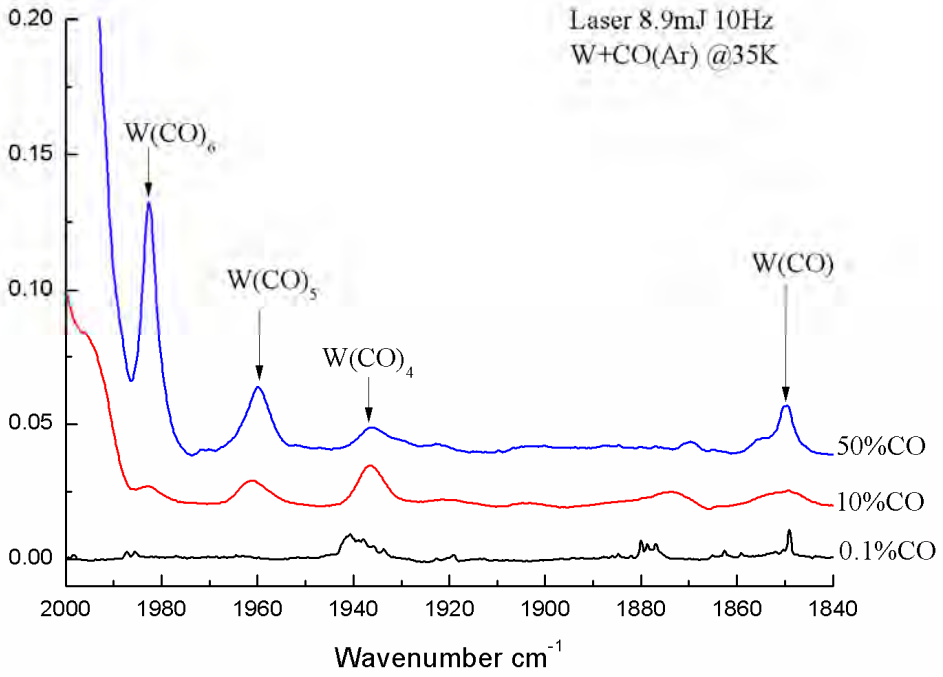


Yields of Mo-carbonyls with different (CO) numbers in various CO concentration

Experimental results

Infrared spectra of W-carbonyls





For 0.025% CO in neon, only WCO and $W(CO)_2$ were observed. But these unsaturated carbonyls readily add CO to produce stable saturated $Mo(CO)_6$ when increase the annealing temperature.

Conclusion

1. The formation of Mo/W-carbonyls is a "cold-atom reaction"

2. In excess CO and inert gas mixture, the free Mo/W atoms will form $Mo/W(CO)_6$ directly and saturated hexacarbonyl complex is the main products.

Prospective

group	VB	VI	VII	VIII		
Element and carbonyls	$V(CO)_6$	$Cr(CO)_6$	$Mn(CO)_5$?	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_5$
			$Mn_2(CO)_{10}$	$Fe_2(CO)_9$		
				$Fe_3(CO)_{12}$	$Co_4(CO)_{12}$	
		$Mo(CO)_6$	$Tc(CO)_5$?	$Ru(CO)_5$	$Rh_2(CO)_3$	
			$Tc_2(CO)_{10}$	$Ru_2(CO)_9$	$Rh_4(CO)_{12}$	
		$W(CO)_6$	$Re(CO)_5$?	$Os(CO)_5$	$Ir_4(CO)_{12}$	
			$Re_2(CO)_{10}$	$Os_2(CO)_9$		
		$Sg(CO)_6$	Bh	Hs	Mt	

1、Laser-ablation matrix-isolation infrared spectroscopic investigation

2、Tc,Ru and Rh carbonyls study using new ^{252}Cf source


Thank you