Laser-induced fluorescence study of Tungsten Oxide (WO)

Jicai Zhang [1,2], Dongmei Zhao [1], Xinwen Ma [1], Jie Yang [1†]

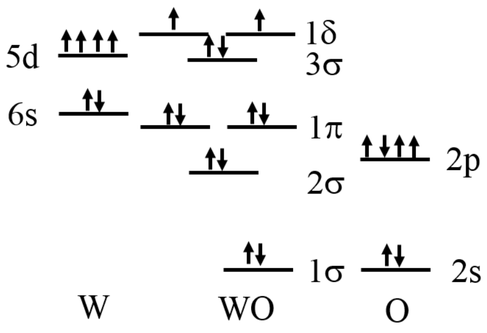
[1]Institute of Modern Physics, Chinese Academy of Sciences, 730000 Lanzhou, China

[2]University of Chinese Academy of Sciences, 100049 Beijing, China

Abstract **The laser-induced fluorescence (LIF) excitation spectra of WO molecule have been recorded in the energy range of 18900 – 23500 cm^{-1} using laser ablation of tungsten target and reaction with free jet expansion of oxygen. Totally 63 vibronic transition bands were observed, and 60 bands were grouped into 10 electronic transition progressions, where 8 electronic transition progressions have the $X0^+$ state as the lower state, as well as 2 progressions have the X1 state as the lower state. Four electronic transition systems $[21.2]0^+ – X0^+$, $[22.2]0^+ – X0^+$, $[21.5]0^+ – X0^+$ and $[23.3]1 – X0^+$ were only identified by LIF spectroscopy. The molecular constants, including rotational constant, vibrational frequency, vibrational anharmonic constant, in the electronic excited states were obtained through rotational analysis of the spectra. In addition, the fluorescence lifetimes of the vibronic states were measured under the collision-free condition by exponentially fitting the fluorescence decay.**

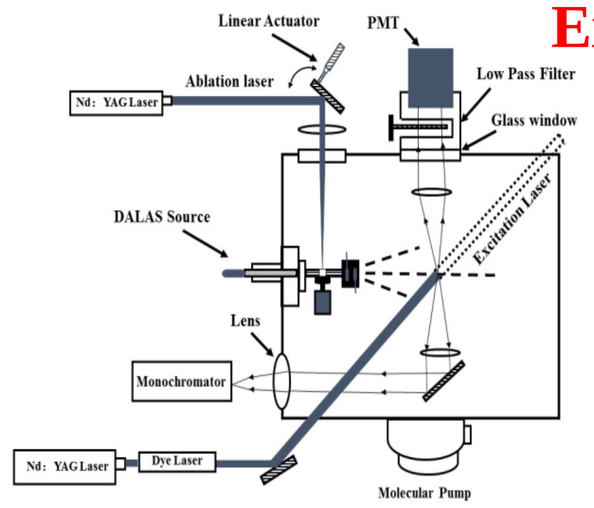
Introduction

WO is a fundamental transition metal containing radical, which has some relevance to material science, catalysis and high-temperature chemistry.



- **Chemical bonding of open 5d shells;**
- **Reprehensive Hund's coupling case (c);**
- **Test quantum chemistry calculation;**

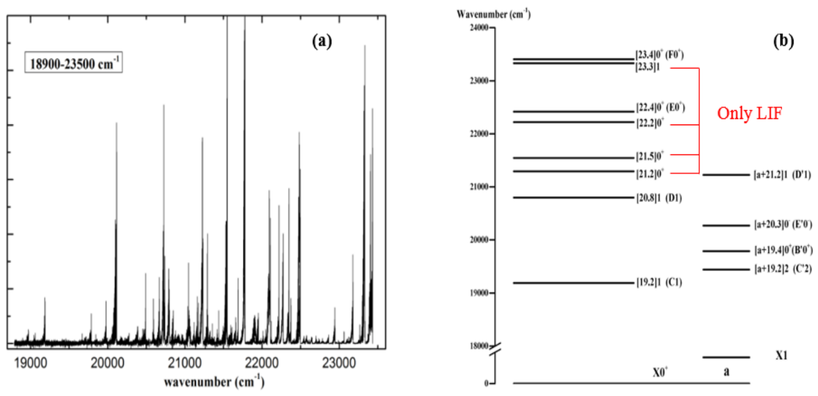
Experiment setup



- **WO radical molecules: discharge assisted laser ablation source;**
- **Excitation laser : pulsed dye laser, linewidth ~0.05cm^{-1}, duration ~5 ns,**

Results

LIF spectra and schematic energy levels of WO in the range of 18900 – 23500 cm^{-1}

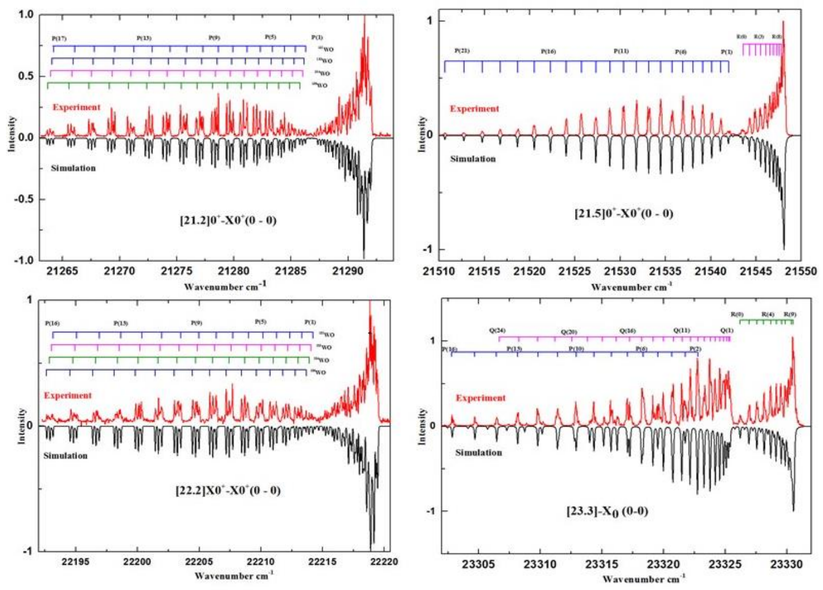


- **Totally 63 vibronic bands observed in LIF.**

60 bands are grouped to 10 electronic progressions, in which 8 have the $X0^+$ state as the lower state, 2 have the X1 state as the lower state.

- **4 upper states $[21.2]0^+$, $[21.5]0^+$, $[22.2]0^+$ and [23.3]1 are only identified in LIF spectra.**
- **2 states $E'0^-$ and $B'0^+$ are only observed in Fourier transform emission (FTE) spectra[1].**

[1]R. S. Ram, J. Mol. Spectrosc. 256, 216 –227 (2009).



Electronic excited states of WO

- **Rotationally resolved v' - v" (0 – 0) bands of the transitions: $[21.2]0^+ – X0^+$, $[21.5]0^+ – X0^+$, $[22.2]0^+ – X0^+$, $[23.3]1 – X0^+$.**
- **The rotational and vibrational constants of all electronic excited states were obtained through rotational analysis of the spectra.**
- **The isotope shifts were observed in the $[21.2]0^+ – X0^+$ and $[22.2]0^+ – X0^+$ (0 – 0) bands, which caused by the perturbation of nearby excited states.**
- **Totally 5 electronic states having the symmetry of 0^+ in experiment, but *ab initio* calculation from Ram *et al.*[1] obtained only two states have the 0^+ symmetry.**
- **The anomalous isotope shifts (IS) were very common in 0-0 band of WO molecule.**

(0-0) band of states	C1	D1	[21.2]	[21.5]	[22.2]	$E0^+$	[23.3]	$F0^+$	C′2	D′1
B (cm^{-1})	0.3917(80)	0.3888(9)	0.3845(1)	0.3856(1)	0.3803(1)	0.384(1)	0.3851(2)	0.3835	0.3881(9)	0.3850(3)
IS (cm^{-1}/amu)	0	0	0.15	0	0.17	~0.01	0	0.1	0	0

Conclusions

The LIF excitation spectra of WO molecule were recorded in the 18900 – 23500 cm^{-1} range, four electronic transitions were newly identified.

- ✓ **The molecular constants in all electronic excited states were obtained;**
- ✓ **Anomalous isotopic shifts were observed in the v' - v" (0 – 0) bands of $[21.2]0^+ – X0^+$ and $[22.2]0^+ – X0^+$ progressions.**
- ✓ **Combining the rotationally resolved LIF and FTE spectra, most low-lying electronic states having the quantum number $\Omega < 3$ have been experimentally identified.**
- ✓ **More *ab initio* calculations are needed for completely understand.**

Acknowledgement

Project supported by the National Key R&D Program of China (Grant No. 2017YFA0402300), the National Natural Science Foundation of China (Grant No. 11404346), and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB21030900).

Authors

* **Jicai Zhang, PhD student, email: zhangjicai@impcas.ac.cn**

† **Jie yang, professor, email: jie.yang@impcas.ac.cn**