Velocity map imaging study on the singlet and triplet dissociation pathway of OCS near 230 nm

XiangKun Wu, Zhi Gao, XiaoGuo Zhou*, ShiLin Liu*

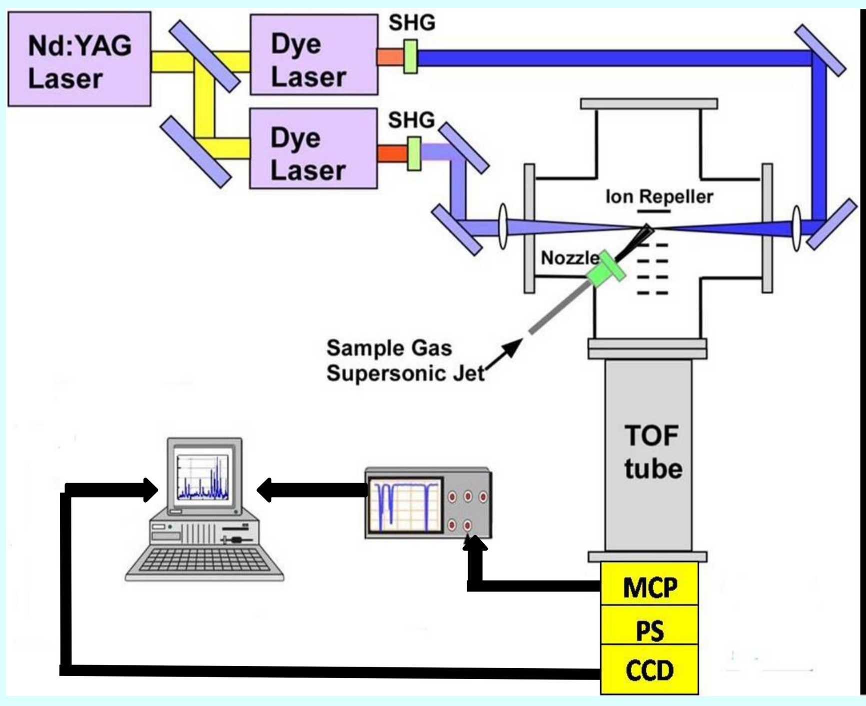
Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

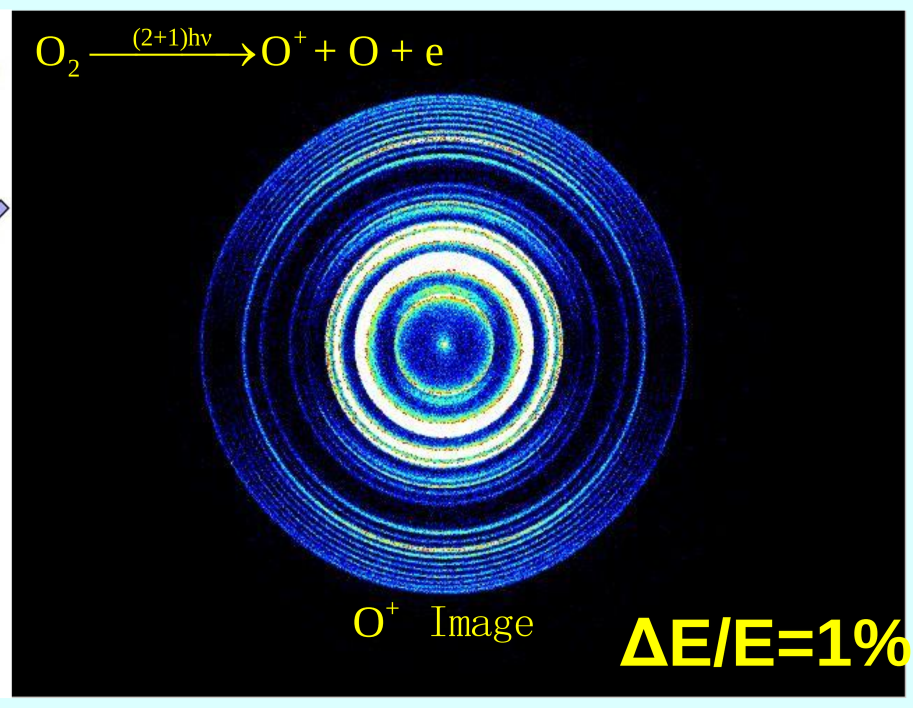
Introduction

Resonance-enhance multiphoton ionization (REMPI) is used to prepare internal state-selected ion, and its dissociation dynamics is investigated using velocity map imaging (VMI) technique, e.g. the kinetic energy and angular distributions.

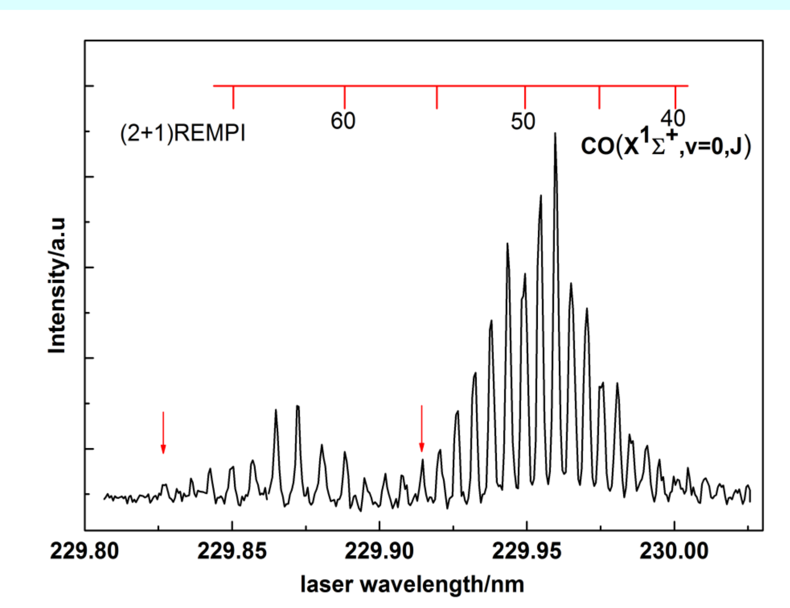
In this experiment, OCS molecule was dissociated by a UV photon at near 230 nm, and then the fragment CO($X^2\Sigma^+$,v=0) was ionized by the same laser via (2+1) REMPI process. The kinetic energy and angular distributions of CO were obtained with VMI. With the aid of the recent theoretical potential energy surface, the dissociation mechanisms of OCS along the singlet and triplet pathways were proposed.

Experiment

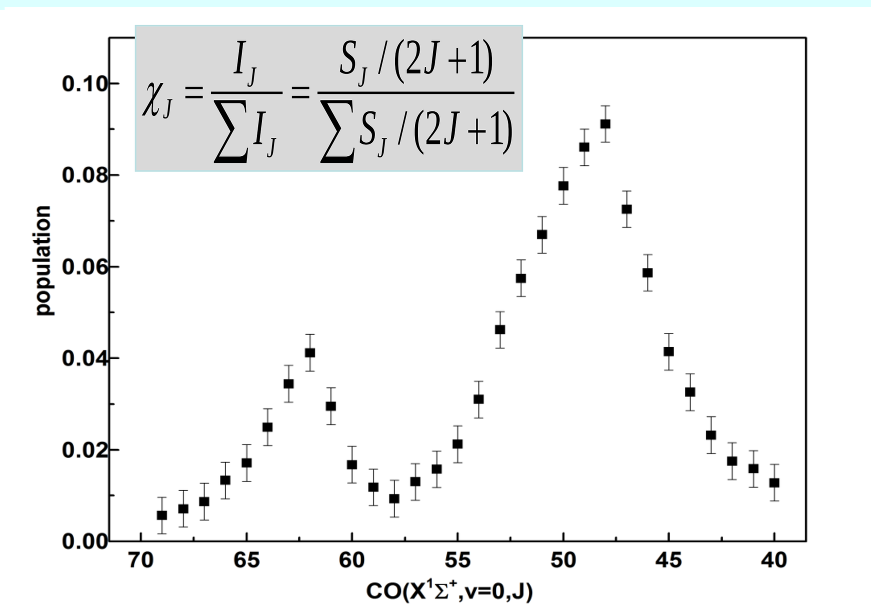




Result and Discussion



CO($X^1\Sigma^+$, v=0,J) fragment (2+1) REMPI spectrum

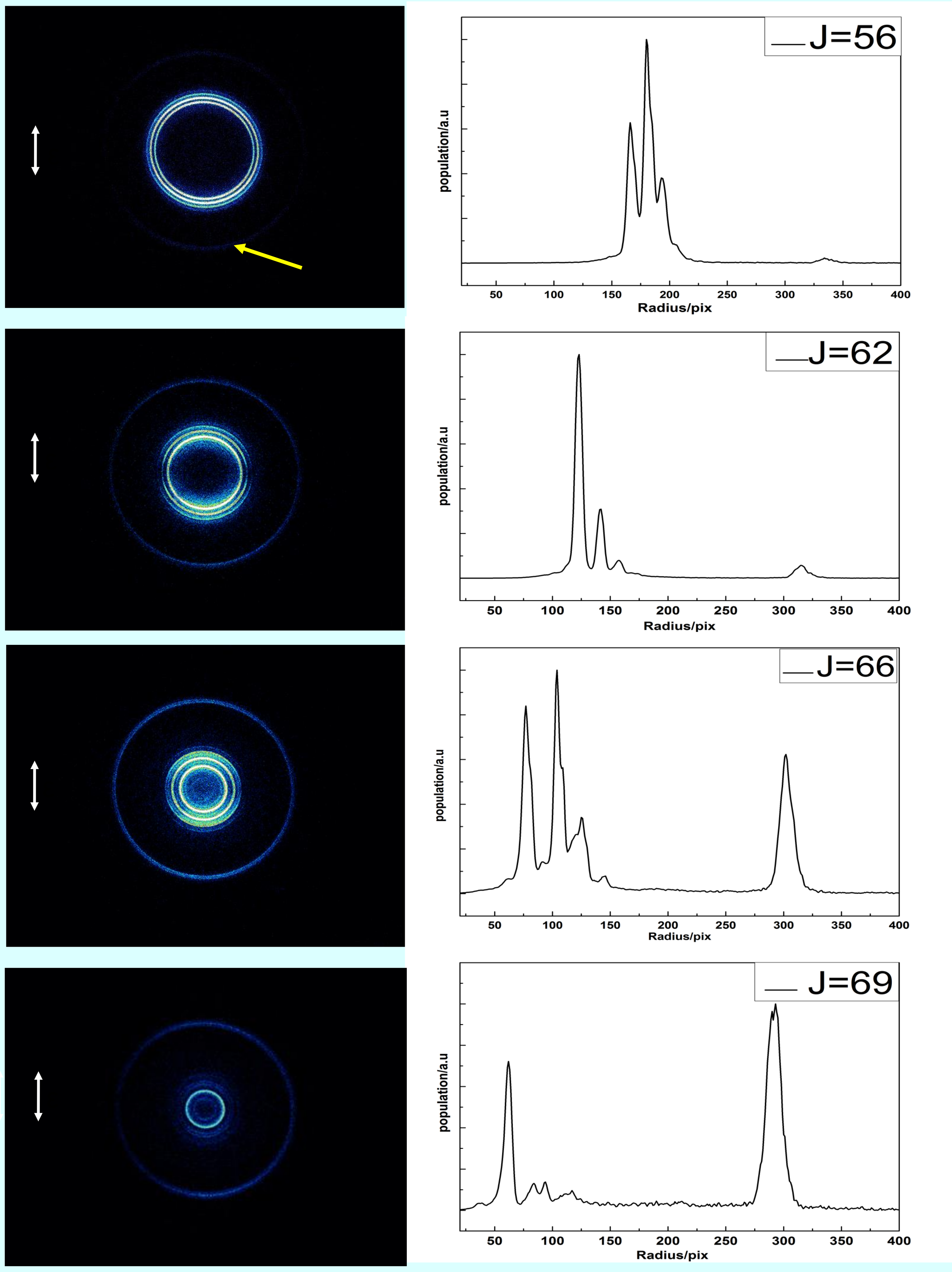


Dissociation fragment CO($X^1\Sigma^+$, v=0, J=40~69) relative intensity

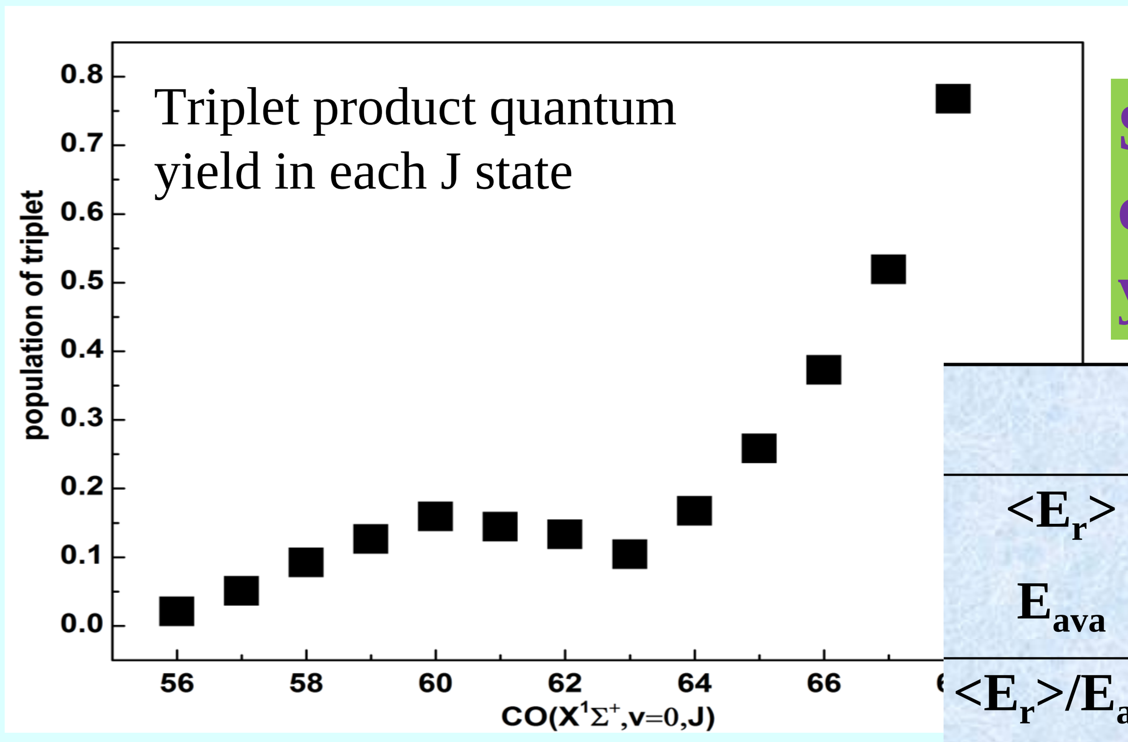
Table: anisotropy parameter of product CO in each rotate state

J	Single					triplet	
	V_2=0		V_2=1		V_2=2		
	This work	EXP a	This work	EXP a	This work	This work	EXP b
56	1.09±0.02	0.92±0.07	0.91±0.01	0.95±0.04	0.74±0.02	1.73±0.17	
57	1.27±0.02	0.95±0.08	1.12±0.02	1.13±0.03	0.83±0.02	1.63±0.13	
58	1.54±0.02	1.41±0.07	1.35±0.02	1.23±0.05	0.92±0.02	1.47±0.07	
59	1.64±0.02	1.51±0.09	1.53±0.02	1.61±0.03	1.10±0.03	1.34±0.08	
60	1.56±0.02	1.69±0.05	1.68±0.02	1.66±0.03	1.34±0.03	1.17±0.06	
61	1.67±0.03	1.65±0.04	1.81±0.04	1.81±0.04	1.60±0.07	1.05±0.09	
62	1.46±0.02	1.75±0.04	1.75±0.04	1.84±0.02	1.60±0.05	1.12±0.07	
63	1.37±0.02	1.50±0.10	1.73±0.03	1.75±0.03	1.77±0.05	1.58±0.10	
64	1.41±0.02	1.64±0.01	1.70±0.03	1.69±0.02	1.71±0.04	1.10±0.05	
65	1.19±0.02	1.42±0.01	1.65±0.03	1.71±0.05	1.71±0.04	0.88±0.04	
66	0.63±0.01	1.17±0.08	1.46±0.02	1.63±0.01	1.50±0.03	0.83±0.03	0.4
67	0.00±0.01	0.98±0.05	1.22±0.02	1.59±0.02	1.46±0.04	0.82±0.02	0.4
68	0.25±0.01		0.76±0.02		1.22±0.04	0.77±0.03	
69			0.00±0.01		0.95±0.05	1.19±0.06	

a) A. J. van den Brom, et. al., *J.Chem.Phys.* 117.4255 (2002)
b) A. Sugita, et. al., *J.Chem.Phys.* 112,7095 (2000)



CO($X^1\Sigma^+$, v=0, J=56,62,66,69) fragment ion imaging and velocity integration distribution

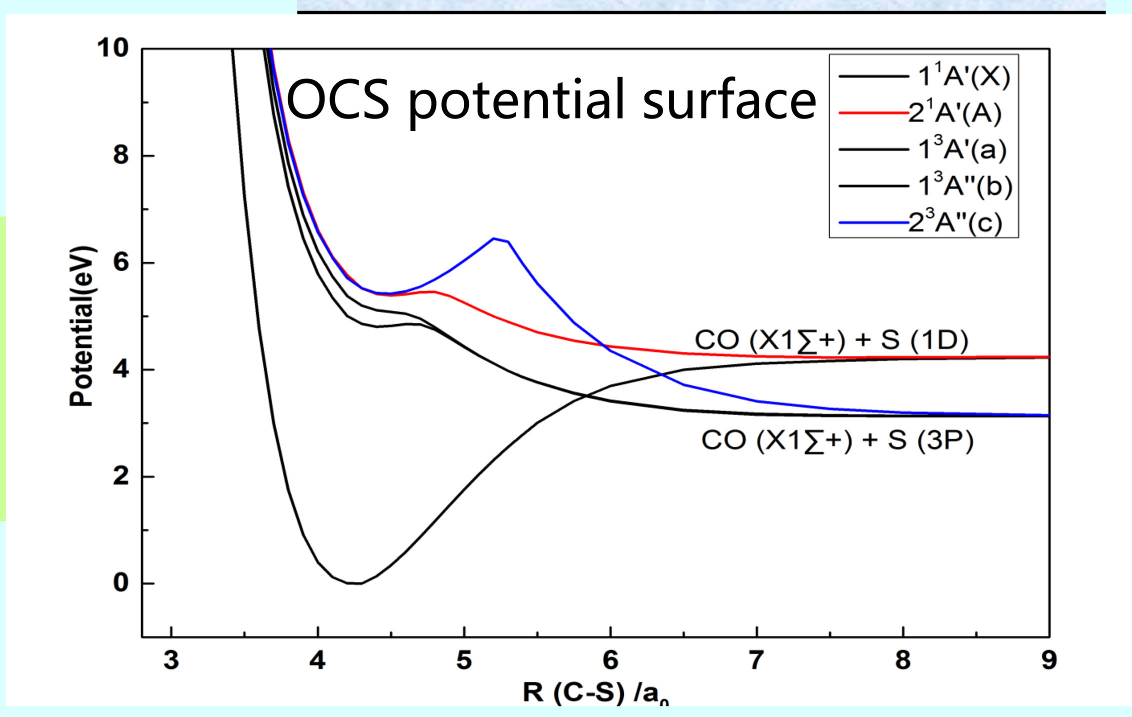


Sum of triplet product channel quantum yield~4.16%

	S (^{1}D)	S(^{3}P)
$\langle E_r \rangle$	0.67eV	0.95eV
E_{ava}	1.11eV	2.25eV
$\langle E_r \rangle / E_{ava}$	62%	42%

Electron state absorption cross section ratio

$\sigma_a/(\sigma_A+\sigma_a)=0.017\%$
$\sigma_b/(\sigma_A+\sigma_b)=0.52\%$
$\sigma_c/(\sigma_A+\sigma_c)=7.46\%$



Schmidt et.al. ,JCP,136,131101 (2012)
Schmidt et.al., JCP,137,054313 (2012)

Conclusion

$$OCS(X^1\Sigma_g^+) \xrightarrow{h\nu} OCS(A^1A') \xrightarrow{spin-orbit\quad coupling} OCS(c^3A'')$$
$$\longrightarrow CO(X^1\Sigma_g^+, v=0, J) + S(^3P)$$

Acknowledge: NSFC. 21373194; "973", 2013CB834602