

31 March 1995

Chemical Physics Letters 235 (1995) 497-502

CHEMICAL PHYSICS LETTERS

# Reaction kinetics of Mo( $a^7S_3$ , $a^5S_2$ , $a^5D_J$ , $a^5G_J$ ) with $O_2$

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Received 9 December 1994; in final form 27 January 1995

#### Abstract

The gas pl. is reactivities of Mo( $a^7S_3$ ,  $a^5S_2$ ,  $a^5D_J$ ,  $a^5G_J$ ) with  $O_2$  in the temperature range 297-620 K are reported. Mo atoms were produced by the photodissociation of Mo(CO)<sub>6</sub> and MoCl<sub>4</sub> and detected by laser-induced fluorescence. The disappearance rates of all states arc found to be pressure independent with argon buffer gas. The disappearance rate constants of the  $s^1d^5 a^7S_3$ ,  $a^5S_2$  and  $a^5G_J$  states are on the order of the gas kinetic rate constant. The  $s^2d^4 a^5D_J$  states are not as reactive and are found to be temperature dependent. Results are discussed in terms of the different electron configurations of the states.

#### 1. Introduction

The gas-phase chemistry of transition-metal (TM) species has received considerable attention [1]. Of particular interest is the influence of the ground and low-lying excited electronic states on the reactivity of TMs in oxidation reactions. It has been suggested that the reactivity of TMs may be correlated with the energy of the lowest lying  $s^{1}d^{n-1}$  electronic state, where n is the number of valence electrons [2]. This difference is presumably due to the energy barrier associated with the  $s^2 d^{n-2} \rightarrow s^1 d^{n-1}$  promotion energy since it is the  $s^1 d^{n-1}$  states which are expected to be correlated to the lowest lying states of the oxide products. Experiments on V [3] and Ti [4] indicate the  $s^2 d^{n-2}$  configuration reacts at a much slower rate than the  $s^1 d^{n-1}$  configuration in reactions involving several oxidants. These experiments, however, are complicated by the additional energy of the  $s^1 d^{n-1}$  configuration over that of the  $s^2 d^{n-2}$ configuration which has an uncertain effect on the reaction dynamics; i.e. the increase in reaction rate may be an energy effect and not due to the different electron configurations.

In an effort to understand the dynamics of TM oxidation reactions, we report here a kinetic study of the oxidation of the ground state  $(5s^14d^5 a^7S_3)$  and three excited terms  $(5s^14d^5 a^5S_2, 5s^24d^4 a^5D_J)$ , and  $5s^14d^5 a^5G_J)$  of molybdenum atoms with molecular oxygen. The energy level diagram for these states is shown in Fig. 1. In the case of Mo, the ground  $s^1d^5 a^7S_3$  state has a lower energy than the  $s^2d^4 a^5D_J$  states, so that energetics should not enhance the reactivity of this state over that of the  $s^2d^4$  configuration. By studying these states of Mo, we can gain a better understanding of how the electron configuration of the TM affects the reaction rate.

## 2. Experimental

Pseudo-first order kinetic experiments ([Mo]  $\ll$  [O<sub>2</sub>]) were carried out in a slowly flowing apparatus using a laser photolysis/laser-induced fluorescence



Fig. 1. Energy level diagram showing all the electronic states of Mo below  $17000 \text{ cm}^{-1}$  excitation energy (Ref. [5]).

(LIF) technique [1]. Mo atoms were produced by the 248 nm photodissociation of  $Mo(CO)_6$  or  $MoCl_4$  with the unfocused output of an excimer laser (Lambda Physics Lextra 200). Kinetic results were independent of photolysis laser fluency (50–200 mJ/cm<sup>2</sup>) and Mo sources. Mo atoms were detected

Table 1 States used for probing molybdenum atoms "

via LIF using an excimer-pumped dye laser (Lambda Physics Lextra 50/ScanMate 2E). LIF excitation and detection wavelengths are given in Table 1. Interference filters (Melles Griot and Corion) were used to isolate the LIF. A photomultiplier tube (Hamamatsu R375) was used in collecting the LIF which was subsequently sent to a gated boxcar sampling module (Stanford Research Systems SR250), and the digitized output was stored and analyzed by a computer.

The reaction chamber and convection oven used in these experiments are similar to those described previously [1]. The Mo precursor was entrained in a flow of argon gas. The diluted Mo precursor, Ar buffer gas, and  $O_2$  flowed through calibrated mass flow meters and flow controllers (MKS types 1459C and 0258C, and Matheson models 8102 and 8202-1423) prior to admission to the reaction chamber. Total flows were between 200 and 3500 sccm. Pressures were measured with MKS Baratron manometers, and chamber temperatures were measured with a thermocouple. Typical precursor pressures were 1 to 100  $\mu$ Torr.

The delay time between the photolysis pulse and the dye-laser pulse was varied by a digital delay generator (Stanford Research Systems DG535) controlled by a computer. The trigger source for these experiments was scattered pump laser light incident upon a fast photodiode. LIF decay traces consisted of

State	Aexcitation	Transition	Detection filter (nm) <sup>b</sup>	Transition detected
a <sup>7</sup> S <sub>3</sub>	386.41	$z^{7}P_{3}^{0}-a^{7}S_{3}$	400	same
	390.30	$z^{7}P_{2}^{0}-a^{7}S_{3}$	400	same
a <sup>5</sup> S <sub>2</sub>	550.65	z 5P3-a 5S5	600	$z^{5}P_{3}^{0}-a^{5}D_{4}$
a <sup>5</sup> D <sub>0</sub>	429,39	$z^{5}F_{1}^{0}-a^{5}D_{0}$	550	$z^{5}F_{1}^{0}-a^{5}G_{2}^{2}$
a <sup>5</sup> D <sub>1</sub>	429.21	$z^{5}F_{2}^{0}-a^{5}D_{1}$	550	$z^{5}F_{0}^{0}-a^{5}G_{0}^{1}$
a <sup>s</sup> D <sub>2</sub>	429.32	z 5Fi-a 5D	550	$z^{5}F_{0}^{0}-a^{5}G_{1}$
a <sup>5</sup> D <sub>3</sub>	428.86	$z^{5}F_{1}^{0}-a^{5}D_{1}^{0}$	550	$z^{5}F_{0}^{0}-a^{5}G_{1}$
a <sup>5</sup> D <sub>4</sub>	427.72	$z^{5}F_{5}^{0}-a^{5}D_{1}$	500	$z^{5}F_{6}^{0}-a^{5}G_{6}$
a <sup>5</sup> G <sub>2</sub>	428.71	x <sup>5</sup> P <sub>2</sub> <sup>6</sup> -a <sup>5</sup> G	550	$x^5 P_0^0 - a^3 D_{2,0}$
$a^{5}G_{3}$	429.66	$x^{5}P_{3}^{0}-a^{5}G_{3}$	550	$x^5 P_0^0 - a^3 D_2$
a 'G	431.51	$y^{5}D_{4}^{0}-a^{5}G_{4}$	500	$v^5 D_0^0 - b^5 D_1$
a <sup>s</sup> G <sub>s</sub>	432.20	$y^{S}D_{1}^{0}-a^{S}G_{s}$	500	$v^{5}D_{v}^{0}-b^{5}D_{v}$
a <sup>s</sup> G <sub>6</sub>	391.11	z <sup>3</sup> H <sub>6</sub> <sup>0</sup> -a <sup>5</sup> G <sub>6</sub>	550	$z^{3}H_{0}^{0}-a^{3}H_{5}$

\* Refs. [5] ar.d [6].

Broad band filter with fwhm = 50 nm.



Fig. 2. Typical Mo decay curves with added O<sub>2</sub>. Data is for Mo( $a^5D_1$ ). Temperature = 295 K, total pressure = 20.0 Torr, Mo(CO)<sub>6</sub> partial pressure = 0.05 mTorr. The solid lines through the data are exponential fits. (a)  $P(O_2) = 47 \text{ mTorr}$ ;  $1/\tau = 0.0196 \text{ } \mu \text{s}^{-1}$ ; (b)  $P(O_2) = 91 \text{ mTorr}$ ;  $1/\tau = 0.0353 \text{ } \mu \text{s}^{-1}$ ; (c)  $P(O_2) = 363 \text{ mTorr}$ ;  $1/\tau = 0.115 \text{ } \mu \text{s}^{-1}$ .

200-800 points, each point averaged over 2-5 laser shots.

#### 3. Results

The decay rates of Mo atoms as a function of  $O_2$ pressure were investigated from 296-620 K at 20 Torr total pressure using argon bath gas. Typical decay plots are presented in Fig. 2. First-order exponential decays of the Mo in the presence of  $O_2$  were observed for the  $a^7S_3$ ,  $a^5D_1$ , and  $a^5G_1$  states. The lines through the data in Fig. 2 are exponential fits from which the pseudo-first order rate constant,  $1/\tau$ , is obtained. The second order rate constant is determined from a plot of  $1/\tau$  versus O<sub>2</sub> pressure. A typical plot for obtaining second order rate constants is presented in Fig. 3; the slope yields the observed bimolecular rate constant. Measured rate constants for the  $a^7S_3$ ,  $a^5D_J$  and  $a^5G_J$  states are listed in Table 2. Those for Mo( $a^7S_3$ ) and Mo( $a^5D_J$ ) at 298 K were collected at total pressures ranging from 10 to 300 Torr for  $a^5D_J$  and from 10 to 100 Torr for a<sup>7</sup>S<sub>3</sub> in Ar buffer gas (they are pressure independent). The quoted uncertainties of  $2\sigma$  represent the sum of statistical scatter in the data and instrumental uncertainties such as gas flow measurements [1]. Results obtained for the a<sup>5</sup>D<sub>0.2.3</sub> spin-orbit states



Fig. 3. Typical plot for determining  $k_{2nd}$ . Data is for Mo(a<sup>5</sup>D<sub>1</sub>). The points at 47, 91, and 363 mTorr O<sub>2</sub> are those obtained from Fig. 2. The solid line is a linear regression fit from which  $k_{2nd} = (9.0 \pm 0.9) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> is obtained.

are not listed in Table 2 but were found to be identical (within experimental uncertainty) to those presented for the  ${}^{5}D_{1}$  spin-orbit state, indicating either rapid interconversion among said states or identical rate constants. Rate constants for the  $a{}^{5}D_{1}$  and  $a{}^{5}D_{4}$  states are compared in Arrhenius form in Fig. 4. Arrhenius expressions are:

$$k(a^{5}D_{1}) = (1.65 \pm 0.22) \times 10^{-10}$$
  
 
$$\times \exp(7.4 \pm 0.5 \text{ kJ mol}^{-1}/RT) \text{ cm}^{3} \text{ s}^{-1}$$
  
 
$$k(a^{5}D_{4}) = (1.22 \pm 0.58) \times 10^{-10}$$
  
 
$$\times \exp(5.7 \pm 1.4 \text{ kJ mol}^{-1}/RT) \text{ cm}^{3} \text{ s}^{-1}$$

where the uncertainties represent  $\pm 2\sigma$ .



Fig. 4. Arrhenius plots for the collisional disappearance of  $Mo(a^5D_1)$  and  $Mo(a^5D_4)$  with  $O_2$ . Error bars represent  $\pm 2\sigma$ . Solid lines are weighted exponential fits to the equation  $k(T) = A \exp(-E_a/RT)$ . See text for results of fit.

The decay behavior of the  $a^{5}S_{2}$  state in the presence of  $O_{2}$  was observed to be biexponential as shown in Fig. 5. To analyze the time-dependence of the  $a^{5}S_{2}$  state, we assumed the following four processes were of primary importance:

$$Mo(a^{5}S_{2}) + O_{2} \xrightarrow{k_{1}} MoO + O$$
 (1)

$$Mo(a^5D_J) + O_2 \xrightarrow{k_2} MoO + O$$
 (2)

$$Mo(a^{5}D_{J}) + O_{2} \xrightarrow{k_{3}} Mo(a^{5}S_{2}) + O_{2}^{*}$$
(3)

$$Mo(a^{5}D_{J}) + Ar \xrightarrow{k_{4}} Mo(a^{5}S_{2}) + Ar^{*}$$
(4)

In this analysis, the reverse processes of (3) and (4) were assumed insignificant (as required by microscopic reversibility) and collisional quenching to the ground state for both terms was assumed negligible. Solution of the resulting two rate equations yields:

$$\begin{bmatrix} {}^{5}S_{2} \end{bmatrix} = \begin{bmatrix} {}^{5}S_{2} \end{bmatrix}_{0} \exp(-k_{1}[O_{2}]t) + \begin{bmatrix} {}^{5}D_{J} \end{bmatrix}_{0}$$

$$\times \left( \frac{k_{3}[O_{2}] + k_{4}[Ar]}{(k_{1} - k_{2} - k_{3})[O_{2}] - k_{4}[Ar]} \right)$$

$$\times (\exp\{-[(k_{2} + k_{3})[O_{2}] - k_{4}[Ar]]t\}$$

$$-\exp(-k_{1}[O_{2}]t))$$
(5)

$$\begin{bmatrix} {}^{5}\mathsf{D}_{J} \end{bmatrix} = \begin{bmatrix} {}^{5}\mathsf{D}_{J} \end{bmatrix}_{0} \exp\left[-\left(k_{\mathrm{r}}[\mathsf{O}_{2}] + k_{4}[\mathsf{Ar}]\right)t\right] \qquad (6)$$



Fig. 5. Typical Mo( $a^5S_2$ ) state biexponential decay curve. Temperature = 296 K, total pressure = 40.0 Torr,  $P(O_2) = 50$  mTorr, Mo(CO)<sub>6</sub> partial pressure = 2 µTorr. The solid line through the data is the biexponential fit in which  $\tau_1 = 8.61$  µs,  $\tau_2 = 55.7$  µs, and A/B = 0.81 (see Eqs. (7) and (8) in text).

Table 2 Measured rate constants for collisions of Mo  $(a^7S_3, a^5S_2, a^5D_J, a^5G_J)$  with O<sub>2</sub>

Mo state <sup>a</sup>	Energy	T (K)	$k \pm 2\sigma$
	(cm <sup>-1</sup> )		$(10^{-11} \text{ cm}^3 \text{ s}^{-1})$
5s14d5 a7S3	0	296-611	10±3
5s <sup>1</sup> 4d <sup>5</sup> a <sup>5</sup> S <sub>2</sub>	10768.33	296-450	$10 \pm 3$
$5s^24d^4 a^5D_J^{b}$	11832 °	296	$0.93 \pm 0.18$
		325	$1.1 \pm 0.2$
		343	$1.3 \pm 0.2$
		372	$1.4 \pm 0.3$
		386	$1.8 \pm 0.3$
		428	$2.1 \pm 0.4$
		457	$2.4 \pm 0.4$
		475	$3.2 \pm 0.5$
		499	$2.8 \pm 0.5$
		548	$3.6 \pm 0.6$
		550	$3.1 \pm 0.5$
		614	$3.8 \pm 0.6$
		620	$4.7 \pm 0.8$
$5s^24d^4 a^5D_1$	11142.83	297	$0.80 \pm 0.16$
·		332	$1.2 \pm 0.2$
		354	$1.4 \pm 0.2$
		358	$1.4 \pm 0.2$
		373	$1.5 \pm 0.2$
		406	$1.8 \pm 0.3$
		423	$2.1 \pm 0.3$
		458	$2.2 \pm 0.3$
		502	$2.8 \pm 0.4$
		549	$3.4 \pm 0.5$
		611	$3.8 \pm 0.6$
5s <sup>2</sup> 4d <sup>4</sup> a <sup>5</sup> D <sub>4</sub>	12346.31	297	$1.8 \pm 0.3$
		339	$2.1 \pm 0.4$
		348	$2.2 \pm 0.4$
		379	$2.5 \pm 0.4$
		398	$2.5 \pm 0.4$
		442	$3.1 \pm 0.5$
		462	$2.9 \pm 0.5$
		471	$3.8 \pm 0.8$
		475	$4.5 \pm 0.8$
		479	$3.1 \pm 0.5$
		502	$3.8 \pm 0.6$
		549	$4.9 \pm 0.8$
		612	5.2 + 0.8
5s <sup>1</sup> 4d <sup>5</sup> a <sup>5</sup> G <sub>J</sub>	16747 <sup>h</sup>	297-378	18±4

<sup>a</sup> Ref. [5].

<sup>b</sup> Determined from monitoring the long time behavior of the  $a^5S_2$  state.

" Weighted average of spin-orbit states.

where  $k_r$  is the J-states averaged removal rate constant due to O<sub>2</sub> for the a<sup>5</sup>D<sub>J</sub> term (=  $k_2 + k_3$ ), [<sup>5</sup>S<sub>2</sub>] represents the time dependent a<sup>5</sup>S<sub>2</sub> state concentration and [<sup>5</sup>D<sub>J</sub>] represents the time dependent a<sup>5</sup>D<sub>J</sub> states concentration. This model yields the requisite biexponential behavior for the  $a^5S_2$  state along with the single exponential behavior observed for the  $a^5D_3$  states. Unfortunately, attempts to fit the  $a^5S_2$ LIF signal versus laser delay experimental data to Eq. (5) were unsatisfactory; i.e. there are too many parameters in Eq. (5) to uniquely determine the rate constants. However, Eq. (5) is of the form:

$$LIF(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$$
 (7)

where LIF(t) represents the laser-induced fluorescence signal of the  $a^5S_2$  state. With only four parameters to fit, the experimental data could be fitted satisfactorily. Fits of the LIF signal versus laser delay to Eq. (7) yielded the short and long temporal time constants,  $\tau_1$  and  $\tau_2$ , respectively, along with the relative amplitude, A/B. The values of  $\tau_1$  and  $\tau_2$  obtained were used to determine removal rate constants for the  $a^5S_2$  and  $a^5D_1$  states, respectively; i.e. the slope of the  $1/\tau_1$  versus O<sub>2</sub> pressure yields the removal rate constant  $(k_1)$  for the  $a^5S_2$  state while the slope of  $1/\tau_2$  versus  $O_2$  pressure yields the removal rate constant  $(k_r)$  for the a <sup>5</sup>D term. The value of the rate constant,  $k_1$ , for the  $a^5S_2$  state was found to be  $(1.0 \pm 0.3) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> and was independent of temperature and Ar buffer gas pressure (10-100 Torr) within experimental uncertainty. The values of  $k_r$  for the  $a^5D_r$  states are listed in Table 2 and represent an average removal constant for all the J states of the  $a^5D_J$  term. The fact that the measured removal rate constants determined indirectly from the decay of the a 5S, state are essentially the same as the rate constants measured directly by monitoring the individual  $a^5D_1$  states is convincing evidence for our model.

From the above analysis we are unable to differentiate between chemical reaction and energy transfer for the  $a^5D_J$  states. However, straightforward manipulation of Eqs. (5) and (7) result in a relationship between the ratio A/B and the individual rate constants:

$$A/B = \frac{\begin{bmatrix} {}^{5}S_{2} \end{bmatrix}_{o}}{\begin{bmatrix} {}^{5}D_{J} \end{bmatrix}_{o}} \left( \frac{k_{1} - k_{2} - k_{3} - k_{4}R}{k_{3} + k_{4}R} \right) - 1$$
(8)

where  $R = [Ar]/[O_2]$ . Note this results in a ratio relationship between rate constants so that one of the values of k is arbitrary. In our analysis, we set  $k_1$  equal to  $1.0 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> and determined the other rate constants relative to this value. A/B ratios for biexponential decays obtained at 296 K for different values of R were used to determine the parameters in Eq. (8). Unfortunately, the values of  $[{}^{5}S_{2}]_{0}/[{}^{5}D_{J}]_{0}$ ,  $k_{2}$ ,  $k_{3}$ , and  $k_{4}$  are not well determined from a fit of the data when all the parameters are allowed to vary independently. A satisfactory fit to the data is obtained, however, if the ratio  $[{}^{\circ}S_{2}]_{0}/[{}^{\circ}D_{J}]_{0}$  is held fixed. In fitting the data to Eq. (8), we made the assumption that the relative production of low lying metastable electronic states from the photolysis event is proportional to the degeneracies of the states produced. This relative population behavior for metastables has been observed previously in experiments utilizing a discharge source for alkaline earth atoms [7,8]. Thus, for analyzing the data the ratio  $[{}^{5}S_{2}]_{0}/[{}^{5}D_{J}]_{0}$  was set to 0.20. With this assumption and with the added constraint that  $k_r$ is equal to  $9 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> determined from  $\tau_2$ values, a satisfactory fit to the data is obtained in which the values of  $k_2$ ,  $k_3$  and  $k_4$  are  $2.4 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>,  $6.6 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> and  $3 \times 10^{-15}$  cm<sup>3</sup>  $s^{-1}$ , respectively. We estimate the uncertainty of these values at  $\pm 50\%$ . Of course, these values are only valid if the value used for  $[a^{5}S_{2}]_{0}/[a^{5}D_{1}]_{0}$ terms is correct; however, it is reassuring that the resulting value of  $k_2$ , the reaction rate constant of Mo( $a^5D_J$ ) with O<sub>2</sub>, is approximately the same as the rate constant for the reaction of the  ${}^{\circ}D_{0}$  ground state of tungsten (the Group 6 metal right below Mo) with  $O_{2}$  [9] in which electronic energy transfer would be expected to be negligible.

### 4. Discussion

The removal rate constants for the ground state  $a^7S_3$  and excited  $a^5S_2$  and  $a^5G_J$  states of Mo in the presence of  $O^2$  are independent of temperature over the indicated ranges and are near the gas kinetic rate constant. Our value for the  $a^7S_3$  state is within the experimental uncertainty of the value determined recently using a flow tube [10]. The production of MoO from Mo( $a^7S_3$ ) and O<sub>2</sub> has an exothermicity of 98.7 kJ/mol [11]. Thus, the most likely product for this reaction is MoO. The rather high reactivity

of the ground state towards  $O_2$  may be due to its orbital correlation with  $2\delta^2 12\sigma^1 6\pi^1 \text{ MoO}(X {}^5\Pi_r)$ [12]. The  $a{}^5S_2$  and  $a{}^5G_J$  states also have rapid removal rates; however, we do not know whether these excited states are quenched by  $O_2$  or MoO is produced.

The bimolecular rate constants for the  $s^2d^4 a {}^5D_J$ states are significantly less than the rate constants for the  $s^1d^5$  states. Bimolecular rate constants for the  $a {}^5D_4$  term are slightly higher than those for the  $a {}^5D_1$ term. We attribute this higher rate constant for the J = 4 state to electronic-to-vibrational energy transfer rather than chemical reaction due to the near resonance between the  $a {}^5S_2 - a {}^5D_4$  energy difference (1578 cm<sup>-1</sup>) [5] and oxygen's fundamental vibrational frequency ( $\omega_0 = 1556$  cm<sup>-1</sup>) [13].

A comparison of the rate constants and Arrhenius parameters for the s<sup>1</sup>d<sup>5</sup> states with the s<sup>2</sup>d<sup>4</sup> a <sup>5</sup>D<sub>j</sub> states indicates the former are more reactive. Based on the s<sup>1</sup>d<sup>n-1</sup> promotion argument, this is expected if MoO is the product formed. The ground state and low-lying excited states of MoO have a single electron in the 12 $\sigma$  molecular orbital. The 12 $\sigma$  orbital in MoO is a nonbonding molecular orbital primarily centered on the metal atom which correlates to the 5s orbital in Mo [12]. Since the s<sup>1</sup>d<sup>5</sup> configuration states do not require promotion of an s electron in the formation of MoO while the s<sup>2</sup>d<sup>4</sup> states do, it is expected the s<sup>1</sup>d<sup>5</sup> configuration states should be more reactive than states with the s<sup>2</sup>d<sup>4</sup> configuration.

#### 5. Summary

We have shown that a ground state TM atom with an  $s^1d^{n-1}$  electron configuration is very reactive lending support for a  $s^2d^{n-2} \rightarrow s^1d^{n-1}$  promotion model. The excited  $s^1d^s \ a^5S_2$  and  $a^5G_4$  states also have large removal rate constants near the gas kinetic value. The  $s^2d^4 \ a^5D_4$  states are significantly less reactive than the ground state despite having over 10000 cm<sup>-1</sup> more electronic energy. Thus, the electron configuration appears to be a dominant factor in the kinetic behavior of gas phase Mo.

## Acknowledgements

This research was supported by an award from Research Corporation and the Naval Academy Research Council.

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