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Reaction dynamics of $AI+O_2 \rightarrow AIO+O$ studied by the crossed-beam laser-induced fluorescence technique

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Dynamics of the reaction, $AI+O_2 \rightarrow AIO+O$, was studied by using the crossed-beam technique at five collision energies from 6.9 to 25.3 kJ/mol. The Al atomic beam was generated by laser vaporization and crossed with the O₂ beam at a right angle. The product AIO was detected by laser-induced fluorescence of the $AIO(B^2\Sigma^+ - X^2\Sigma^+)$ transition and the rotational-vibrational distributions were determined. The observed rotational and vibrational distributions displayed greater populations in lower vibrational and rotational levels than expected statistically. Rotational distributions were also determined for two spin–orbit states of Al, $AI({}^2P_{1/2})$ and $AI({}^2P_{3/2})$, at two collision energies. At a collision energy of 12.2 kJ/mol, the higher energy spin–orbit excited state, $AI({}^2P_{3/2})$, showed lower reactivity, i.e., about one-third of the ground spin–orbit state, $AI({}^2P_{1/2})$. However, the rotational distributions for the two states were almost identical. Both the reactivity and rotational distributions for $AI({}^2P_{1/2})$ and $AI({}^2P_{3/2})$ became similar at a higher collision energy, 18.5 kJ/mol. These results suggest that the reaction of Al with O₂ proceeds via an intermediate complex. Both spin–orbit states lead to the complex, lose memory of the initial electronic state, and provide identical rotational distributions. © 2003 American Institute of Physics. [DOI: 10.1063/1.1591177]

I. INTRODUCTION

One characteristic of metal atom reactions originates from the presence of low-lying electronically excited states. Typical examples are provided by the gas-phase transition metal atoms which usually have several low-lying electronically excited states. Once the transition metal atoms interact with reactant molecules, the potential energy surfaces evolved from these states couple with one another. Therefore, information about the interaction among these surfaces is essential for understanding the reaction dynamics of the reactions of the transition metal atoms. Since the coupling between electronic states can be easily mediated by the collisions with nonreactive atoms or molecules, experimental information derived from multiple collision conditions such as in flow experiments provides only qualitative knowledge about the dynamics of the metal atom reactions.

We have studied the reactions of the first row transition metal atoms with simple molecules, and various important information has been accumulated.^{1–5} However, this information is more or less qualitative with respect to the interaction potential surfaces and dynamics on them because of the limitation of the experimental technique we used, i.e., the multiple collisions with buffer gas species. One experimental approach to obtain detailed information about the interaction potentials is the crossed-beam technique, which has been applied for reactions of transition metal atoms.^{6–8} In order to extend our previous kinetic studies, a new crossed-beam apparatus has been constructed to study the reaction dynamics of gas-phase transition metal atoms, and we selected the following reaction as the first system to be studied by this apparatus,

Al(²P_{1/2,3/2}) + O₂(X³Σ_g⁻)
→ AlO(X²Σ⁺) + O(³P_J)

$$\Delta_{r}H_{0}^{0} = -14.96 \text{ kJ/mol}^{9}.$$
 (1)

The oxidation reactions of aluminum atoms are of considerable interest in studies of combustion, since aluminum compounds are frequently used as an ingredient in propellant formulations.¹⁰ However, the interest in combustion is not centered on reaction (1) but the oxidation to form much more stable products, AlO₂ and Al₂O₃. The exothermic reaction (1), which is the only possible pathway under single collision conditions, has a large rate constant at room temperature, and a negative temperature dependence of the rate constant has been reported.¹¹ The dynamics of this reaction has also been experimental¹²⁻¹⁷ studied and from theoretical viewpoints.¹⁸⁻²⁰ However, only little information has been available for the potential energy surface of this reaction until the recent multiconfigurational study carried out by Pak and Gordon.²¹

Naulin and Costes have studied this reaction by using a crossed beam technique combined with the laser-induced fluorescence detection of product AlO.¹⁷ A variable angle crossed beam apparatus enabled them to determine the reaction cross section as a function of collision energy between 6–255 meV (corresponding to the range from 0.6 to 24.6 kJ/mol). As expected from the negative temperature dependence of the rate constant, the reaction cross section has been observed to decrease monotonically with increasing collision energy. One interesting issue is the reactivity of the excited spin–orbit state, Al(${}^{2}P_{3/2}$), which lies 112.04 cm⁻¹ above

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FIG. 1. Schematic diagram of the crossed-beam apparatus.

the ground spin-orbit state, $Al({}^{2}P_{1/2})$.²² Spin-orbit selective reactivity was first reported by Chen et al.¹⁶ They used a fluorescence-imaging technique in a crossed-beam experiment and observed that only ground state, $Al({}^{2}P_{1/2})$, reacts with O₂. This selectivity was explained by an electrostatic interaction model. Naulin and Costes determined relative cross sections of two spin-orbit components at various collision energies. They used two carrier gases, N₂ and Ne, for the Al beam. The populations of the two spin-orbit states of Al are drastically different in these carrier gases while they provide identical Al mean velocity, i.e., the same collision energy. The relative cross sections determined under two conditions were converted to those for two spin-orbit states. The results showed that the spin-orbit excited state, Al(${}^{2}P_{3/2}$), reacted with O₂ but was less reactive than the ground state, $Al({}^{2}P_{1/2})$, at low collision energies. The relative cross section of $Al({}^{2}P_{3/2})$ increased with collision energy. These results were consistent with the theoretical study based on the adiabatic capture centrifugal sudden approximation (ACCSA) method on the long-range interaction potential made of the quadrupole-quadrupole and dispersion interactions.19

In the present study, we wish to present recent experimental results obtained from our new crossed-beam apparatus. Laser-induced fluorescence is applied to detect the product AlO. Rotational and vibrational distributions of product AlO are determined at five collision energies between 6.9 and 25.3 kJ/mol. The product rotational and vibrational distributions are also determined for two spin-orbit states, $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$. The latter information is expected to be sensitive to the interaction potential and reaction mechanism for each spin-orbit state. Based on these distributions and energy partitioning, the mechanism of reaction (1) is discussed.

II. EXPERIMENT

A. Apparatus

The experiment was carried out by using a crossed-beam apparatus shown in Fig. 1. The apparatus consists of three parts which are differentially pumped. Al atoms were generated by laser vaporization. The second harmonic or fourth harmonic of a YAG laser (Spectra Physics GCR-150-10) was focused onto an Al rod (99.999% purity Al or Al alloy with

TABLE I. Summary of the properties of the Al beam.

Carrier gas	$\langle v \rangle / m/s$	$N[Al(^{2}P_{1/2})]/N[Al(^{2}P_{3/2})]$	$E_{\rm coll}/\rm kJ/mol$	
Kr	610	55/45	6.9	
Ar	870	50/50	9.7	
N_2	1045	90/10	12.2	
Ne	1045	50/50	12.2	
25% N ₂ /He	1400	75/25	18.5	
30%Ne/He	1400	55/45	18.5	
10% N ₂ /He	1700	70/30	25.3	

4% Mg) which was rotated and translated by a stepping motor. Typical laser intensity was 0.8 mJ/pulse and a 500 mm focal length lens was used. Vaporized Al atoms were cooled and issued as an atomic beam by the carrier gas flow expanded from a pulsed valve (Jordan PSV, 1.0 mm diam). The oxygen molecular beam was generated from another pulsed valve (General Valve 9-series, 0.5 mm diam). Pure oxygen was used for all measurements. Both beams were collimated by skimmers (Beam Dynamics, 2 mm diam) and crossed each other at a right angle in the reaction chamber. The metal atomic beam source, the O2 beam source, and the reaction chamber were pumped by 6 in., 10 in., and 6 in. diffusion pumps (Edwards, Difstak), respectively. When both beams were operated, typical background pressures of the source chambers and reaction chamber were 1×10^{-5} and 4 $\times 10^{-6}$ Torr, respectively.

The Al beam and the reaction product AlO were detected by the laser-induced fluorescence technique. For detection of Al, Al $({}^{2}S - {}^{2}P_{1/2,3/2})$ transitions, 394.513 and 396.265 nm, were excited by frequency doubled output of a titaniumsapphire laser (Continuum TS-60) pumped by a YAG laser (Continuum NY-82). Total fluorescence was collected by a lens system and detected by a photomultiplier tube (HAMAMATSU R928). For the AlO detection, the AlO($B^{2}\Sigma^{+}-X^{2}\Sigma^{+}$) transition was used for the LIF. The $\Delta v = 1$ sequence of this transition was excited by a dye laser (Lambda Physik, SCANmate using LC4700 as a dye) pumped by a XeCl excimer laser (Lambda Physik, COMPex 100). A short wavelength cutoff filter (HOYA Y-48) was used to eliminate intense signal from scattered laser photons. After the filter, the fluorescence was detected by the photomultiplier tube. The output of the photomultiplier tube was amplified by a preamplifier (Ortec VT120B) and fed into a gated integrator (SRS SR-250). The excitation laser intensity was measured by a fast photodiode and its signal was also averaged by another gated integrator. The averaged signals of the fluorescence and laser intensity were stored in a computer for further analysis.

Some properties of the Al beam were determined by using the LIF detection of atomic transitions. Relative populations of the two spin-orbit states were determined by the intensities of the LIF signals for the $Al({}^{2}S-{}^{2}P_{1/2,3/2})$ transitions. The velocity distribution of the Al beam was determined by the LIF intensity as a function of the time between the vaporization laser pulse and the detection laser pulse. The relative populations of $Al({}^{2}P_{1/2,3/2})$ and mean velocities of Al are summarized in Table I. The velocity of the O₂ beam was determined by a fast ionization gauge (Beam Dynamics,



FIG. 2. Laser-induced fluorescence spectrum of AlO formed by the reaction, $Al+O_2 \rightarrow AlO+O$. The spectrum was measured at the collision energy of 12.2 kJ/mol.

FIG-1). The peak velocity of O_2 was 760 m/s and the width was about 7%. Collision energies calculated from velocities of both beams are also summarized in Table I.

B. AIO in the primary beam

The laser vaporization Al beam source was found to generate a small amount of AlO. Although several kinds of Al rods, different purities of Al and alloys with Mg, were tried, no significant difference was observed. Two wavelengths of the vaporization laser, 266 and 532 nm, also showed no difference. An in-line gas purifier (Puron 6P-05-N2-N2) reduced the AlO signal, however its effect was not enough to eliminate AlO completely. Therefore, we had to eliminate the contribution of AlO in the Al beam by a subtraction method. That is, the O₂ beam was operated with 5 Hz, while the Al beam containing a small amount of AlO was operated with 10 Hz. The 5 Hz signal synchronized with the O_2 beam and that synchronized without O₂ were averaged independently by two gated integrators and accumulated by a computer. The difference of two spectra was obtained by simple subtraction. Because AlO in the Al beam is populated in low rotational levels of the vibrational ground state, the subtraction was essential to determine the distribution of these levels.

III. RESULTS

A. LIF spectra of AIO($B^2\Sigma^+ - X^2\Sigma^+$) and rotational-vibrational distribution

A typical LIF spectrum of AlO is shown in Fig. 2. This spectrum was obtained by the subtraction method described in the previous section. The collision energy for this spectrum was 12.2 kJ/mol and vibrational levels of AlO up to v = 2 are energetically accessible. Assignment of each line was given by spectroscopic constants available for *B* and *X*

states of AlO²³ and also shown in this figure. The spectrum is similar to those observed by Naulin and Costes at similar collision energies.^{14,17}

The transition line intensities were converted to the rotational distributions. Because the B-X transition of AlO has a large absorption coefficient, the effect of saturation of the absorption must be taken into account. Figure 3 shows the LIF intensities of AlO as a function of the laser intensity measured by the photodiode. Measurements were carried out at the R-head [around R(14)] and P(32) line of the 1–0 band. Both intensities showed nonlinear dependence and it is clear that the absorption of AlO was partially saturated at the laser intensity used (indicated by the arrow in Fig. 3). The effects of the saturation for the population determined by the LIF measurement have been described by Altkon and Zare by using the directional Eistein coefficients.²⁴ There might be some polarization of the rotational angular momentum of the reaction product, AlO, with respect to a space-fixed frame under the crossed-beam conditions. However, since no information about the polarization is available, we assumed that the rotational angular momentum of AlO is isotropically distributed in the space-fixed frame. Under this condition, the



FIG. 3. The intensities of LIF measured as a function of laser intensity.

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relationship between the rotational state population and the LIF intensity can be derived from the rate equation approach based on a two-level model, which is described in the Appendix. As described in the Appendix, the population of the J''th rotational state, $N_{J''}$, divided by its degeneracy, 2J'' + 1, is related to the LIF intensity, I_{LIF} , of the *P* or *R* branch by the following equations:

For the *P*-branch:
$$\frac{N_{J''}}{2J''+1} \propto \frac{I_{\text{LIF}}}{J''\rho^n}$$
;
For the *R*-branch: $\frac{N_{J''}}{2J''+1} \propto \frac{I_{\text{LIF}}}{(J''+1)\rho^n}$.

Here, ρ is the density of radiation, and $I_{\rm LIF}$ has the *n*th power dependence on ρ , i.e., n=1 corresponds to linear dependence and n=0 corresponds to the full saturation condition. These equations indicate that the saturation of absorption affects only the dependence of $I_{\rm LIF}/J''$ or $I_{\rm LIF}/(J''+1)$ on the radiation density, ρ . Because the variation of the laser intensity is small over the LIF spectrum in the present study, $N_{J''}/(2J''+1)$ is proportional to $I_{\rm LIF}/J''$ (for the *P*-branch) or $I_{\rm LIF}/(J''+1)$ (for the *R*-branch), no matter how the absorption is saturated.

At each collision energy, several spectra were measured and averaged rotational distributions are summarized in Fig. 4. Except for the lowest collision energy, 6.9 kJ/mol, the vibrational level of v=2 is energetically possible. (v=3 is also possible for the highest collision energy.) However, just the rotational distributions of v = 0 and 1 are shown in this figure, because not enough transitions were observed for the rotational state distribution of v = 2. Also shown in this figure are rotational distributions expected from statistical energy partitioning which were estimated by $N^0(v,J) \propto (2J)$ $(+1)(E_{av}-E_v-E_r)^{1/2}$, where E_{av} , E_v , and E_r are total available energy of reaction, vibrational energy of AlO, and its rotational energy, respectively. Rotational distributions determined at several collision energies summarized in this figure are quite similar each other. At all collision energies, the populations were observed until the highest energetically possible rotational levels. The observed rotational distributions have a little more population in low rotational levels and relatively less population in high rotational levels than $N^0(v,J)$ in both vibrational states, v=0 and 1.

In Figs. 3(e), 3(f), 3(g), and 3(h), the rotational distributions determined for two different Al conditions are shown. Under these conditions, the relative populations of two spin– orbit states of Al are different, while the collision energies are identical. It is clear that no remarkable difference of rotational distribution is seen between the two Al beam conditions.

In the analysis applied to obtain the rotational distribution, each rotational line was identified and its intensity was converted to the population. However, several rotational lines, especially the transitions originating from low rotational states, were so congested that their intensities could not be obtained directly from the peak height. In order to determine the vibrational distribution, the observed spectra were simulated by using the surprisal parameter and popula-



FIG. 4. Rotational state distributions of AlO (v = 0 and 1) formed by the reaction, Al+O₂ \rightarrow AlO+O. Collision energies were 6.9 kJ/mol [(a) and (b)], 9.7 kJ/mol [(c) and (d)], 12.2 kJ/mol [(e) and (f)], 18.5 kJ/mol [(g) and (h)], and 25.3 kJ/mol [(i) and (j)].

tions of vibrational states as adjustable parameters. In this analysis, the rotational distributions of all vibrational states were assumed to be characterized by a single surprisal parameter, θ , and the distribution was given by $P(v,J) \propto (2J + 1)(E_{av} - E_v - E_r)^{1/2} \exp(-\theta E_r)$. The Franck–Condon factors were taken from the calculation by Michels.²⁵

One example of the simulated spectrum is shown in Fig. 5. This observed spectrum was measured for Al with 30% Ne in He of the carrier gas, i.e., 18.5 kJ/mol of collision energy. The best fit surprisal parameter was θ =1.3, slightly non-statistical, and relative populations of v = 0, 1, and 2 levels were 1.00, 0.27, and 0.06, respectively. Again several spectra were analyzed and vibrational populations were averaged.

B. Energy partitioning

Rotational and vibrational energy partitions are summarized in Table II and Fig. 6. Averaged rotational and vibrational energies based on the statistical energy partitioning are also shown in this table and figure. The observed rotational energies were around 30% of the available energies at low collision energies, and decreased to about 20% at the highest collision energy. These results were common for v = 0 and 1 vibrational states. On the other hand, those expected from the statistical energy partitioning were 40% at all collision ener-

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FIG. 5. Observed and simulated spectra of AlO. The measurement was carried out at 18.5 kJ/mol of collision energy and the spectrum was simulated for the available energy of 2800 cm^{-1} .

gies. As expected from the rotational state distribution, the energy partitioning into rotation of AlO is lower than statistical.

The observed vibrational energies were around 10% of the total available energy and showed no strong dependence on the collision energy. The statistical energy partitioning predicts that slightly greater energy goes into the vibrational motion of AlO and the branching increases with the collision energy. At all collision energies, the vibrational energy partitioning observed was slightly smaller than statistical.

C. Rotational state distribution for each spin-orbit state

As we described in the Introduction, an understanding of the reactivity of the two spin–orbit states of Al, $Al({}^{2}P_{1/2})$

Carrier g	as		Kr	Ar	Ne	N_2	25% N ₂ / He	30%Ne/ He	10% N ₂ / He
$\overline{E_{\rm coll}(\rm kJ/mol)}$		6.9	9.7	12.2	12.2	18.5	18.5	25.3	
E_{avail} (kJ/mol)		21.9	24.7	27.2	27.2	33.5	33.5	40.3	
$N_{1/2}:N_{3/2}$		55:45	50:50	50:50	90:10	73:27	54:46	70:30	
$\langle E_{rot} \rangle$ cm ⁻¹	v = 0	Obs.	617 ± 29	681 ± 68	677 ± 50	668 ± 41	711 ± 30	734 ± 32	783 ± 23
			(33.7%)	(33.0%)	(29.8%)	(29.4%)	(25.4%)	(26.2%)	(23.3%)
		PD^{a}	735	828	911	911	1120	1120	1352
			(40.1%)	(40.1%)	(40.1%)	(40.1%)	(40.0%)	(40.0%)	(40.2%)
	v = 1	Obs.	264 ± 14	346 ± 62	396±26	404 ± 17	556 ± 29	545 ± 57	543 ± 45
			(30.5%)	(31.5%)	(30.4%)	(31.0%)	(30.3%)	(29.7%)	(22.6%)
		PD^{a}	347	441	521	521	735	735	964
			(40.1%)	(39.6%)	(39.9%)	(39.9%)	(40.0%)	(40.0%)	(40.1%)
	v = 2	Obs.	•••	40 ± 2	115±9	113±13	285 ± 9	284 ± 13	421 ± 11
				(27.3%)	(32.5%)	(32.0%)	(32.3%)	(32.2%)	(29.0%)
		PD^{a}		58	142	142	353	353	581
				(39.6%)	(40.2%)	(40.2%)	(40.0%)	(40.0%)	(40.1%)
$N_{\rm vib}/N_0$	v = 1	Obs.	$0.21\pm$	$0.33 \pm$	$0.26 \pm$	$0.25\pm$	$0.35\pm$	$0.29 \pm$	$0.35\pm$
			0.05	0.05	0.04	0.04	0.05	0.04	0.05
		PD^b	0.33	0.39	0.44	0.44	0.54	0.54	0.61
	v = 2	Obs.		$0.012 \pm$	$0.017 \pm$	$0.019 \pm$	$0.072 \pm$	$0.051\pm$	$0.072 \pm$
				0.008	0.008	0.001	0.004	0.012	0.004
		PD^{b}	•••	0.019	0.063	0.063	0.18	0.18	0.29
$\langle E_{\rm vib} \rangle$	Ol	os.	167 ± 34	247 ± 23	228 ± 35	225 ± 26	264 ± 50	267 ± 50	336±16
cm^{-1}			(9.1%)	(12.0%)	(10.0%)	(9.9%)	(9.4%)	(9.5%)	(10.0%)
	PD^{a}		238	294	362	362	502	502	670
			(13.0%)	(14.3%)	(16.0%)	(16.0%)	(17.9%)	(17.9%)	(19.9%)

TABLE II. Summary of energy partition.

^aAverage energy appears as the product rotation or vibration calculated by statistical energy partitioning. ^bStatistical vibrational population.

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FIG. 6. Summary of energy partitioning into rotation (f_r) and vibration (f_v) of AlO.

and Al(${}^{2}P_{3/2}$), is needed to clarify the mechanism of reaction (1). Experimentally, Naulin and Costes have opened the way to determine the cross sections for specific spin–orbit states.¹⁷ The laser vaporization generates both spin–orbit states, however the carrier gas containing N₂ effectively quenches the excited Al(${}^{2}P_{3/2}$) state. Therefore, the Al beam of N₂ containing carrier gas is expected to provide mostly the ground state Al(${}^{2}P_{1/2}$). Since rare gases are not efficient to quench the excited state, the Al beams of rare gases pro-

vide both states. The relative populations of the two states can be determined by the LIF of Al, and then one can convert the cross sections determined by using two different carrier gases, one containing N_2 and the other without N_2 , to those for two spin–orbit states.

We have applied this technique to determine the rotational state distributions for two spin-orbit states. The populations of each rotational state determined using two different Al beam conditions, N(J,A) and N(J,B), can be given in terms of the populations of two spin-orbit states at these beam conditions, $P_{1/2}(A)$, $P_{3/2}(A)$, $P_{1/2}(B)$, and $P_{3/2}(B)$, and the rotational populations generated from two spin-orbit states, $N_{1/2}(J)$ and $N_{3/2}(J)$, by the following equation:

$$\binom{N(J,A)}{N(J,B)} = \binom{P_{1/2}(A)P_{3/2}(A)}{P_{1/2}(B)P_{3/2}(B)} \binom{N_{1/2}(J)}{N_{3/2}(J)}.$$
 (2)

Therefore, the rotational populations determined experimentally can be converted to those for the spin–orbit states by

$$\binom{N_{1/2}(J)}{N_{3/2}(J)} = \binom{P_{1/2}(A)P_{3/2}(A)}{P_{1/2}(B)P_{3/2}(B)}^{-1} \binom{N(J,A)}{N(J,B)}.$$
 (3)

Measurements were carried out at two collision energies, 12.2 and 18.5 kJ/mol. Two carrier gases were used at each collision energy. As already shown in Table I, pure Ne and pure N₂ provided identical mean velocity of Al with different populations of the spin–orbit states, i.e., $Al({}^{2}P_{1/2})/Al({}^{2}P_{3/2})$ is 50/50 in Ne or 90/10 in N₂. Ne and N₂ were diluted by He to increase the mean velocity. These mixtures again provided two substantially different populations of the two states, i.e., $Al({}^{2}P_{1/2})/Al({}^{2}P_{3/2})$ is 55/45 in Ne/He or 75/25 in N₂/He. Because the populations of spin–orbit states were slightly different from day to day, they were measured prior to and after the LIF spectrum measurements of the reaction product AlO. Several measurements were averaged and results are summarized in Fig. 7. Also shown in these figures are the ratios of $N_{3/2}(J)/N_{1/2}(J)$ as a function of rotational energy.



FIG. 7. Rotational state distributions of AlO formed by the reaction, $Al(^2P_{1/2,3/2})+O_2 \rightarrow AlO+O$. Collision energies were 12.2 kJ/mol [(a)] and 18.5 kJ/mol [(c) and (e)]. Also shown are ratios of rotational populations formed from the two spin–orbit components, $N_{1/2}/N_{3/2}$.

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At the collision energy of 12.2 kJ/mol, the rotational populations of AlO from the higher energy Al(${}^{2}P_{3/2}$) are systematically lower than those from the ground state, $Al({}^{2}P_{1/2})$. However, there is no significant difference between the rotational distributions for $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$. The similarity of the distributions is also clear in Fig. 6(b). The ratios seem to remain almost constant in spite of large fluctuations. The averaged ratio was 0.33 ± 0.11 , which is consistent with the ratio of reaction cross sections for two spin-orbit states determined by Naulin and Costes at the same collision energy.¹⁷ At higher collision energy, 18.5 kJ/mol, the rotational distributions were also quite similar each other [Figs. 6(c) and 6(e)]. The averaged ratios of $N_{3/2}(J)/N_{1/2}(J)$ are 0.96±0.60 and 0.98±0.73 for v=0 and 1 vibrational levels, respectively. The increase of these ratios with the collision energy is also consistent with the results obtained by Naulin and Costes.

IV. DISCUSSION

A. Energy partitioning

The rotational and vibrational state distributions for reaction (1) were first determined by Dagdigian et al.¹³ The LIF method was applied in a beam-gas arrangement and the internal state distributions were compared with those calculated from phase space theory. They concluded that the partitioning of energy was not completely statistical at a mean collision energy of 12.6 kJ/mol. Pasternack and Dagdigian also studied the same reaction by using a velocity-selected beam condition and observed a significant deviation from statistical energy partitioning in product rotation at three collision energies from 4.2 to 35.1 kJ/mol.¹² The surprisal parameters they determined for v=0 and 1 levels were negative, which indicated that the experimental rotational distribution populates lower rotational levels than expected statistically. In their crossed-beam study, Costes et al. observed completely statistical energy partitioning at low collision energies, 8.0 and 18.3 kJ/mol, and a slight deviation from the statistical prediction at higher collision energies, 28.0 and 47.3 kJ/mol.

The energy partition determined in the present study shows that both rotational and vibrational energies of AlO are a little lower than those expected from statistical energy partitioning. This result agrees with the observation by Pasternack and Dagdigian. The rotational energy partitioning determined here was around 30%, which is the same as their value. Although the rotational energy partitioning determined by Costes et al. was slightly higher at low collision energies, 35% and 33%, the difference seems to be minor. At higher collision energies, the present results are consistent with those of Costes et al., i.e., the energy partitioning deviates from the statistical expectation. One possible explanation for the minor discrepancy between our results and those of Costes et al. might be inelastic collisions of AlO in the Al beam in our experiment. The rotationally inelastic collisions of AlO in the Al beam may contaminate the population of low rotational states. Because O₂ is reactive with Al to form AlO, it is difficult to estimate the effect of the rotational inelastic collision with O_2 directly. Instead of O_2 , we measured the contribution of the inelastic collisions with NO which is unreactive with Al. Only a little change was observed in the LIF spectrum of AlO when the NO beam was crossed with the AlO containing Al beam. Since this change was negligible compared with the original AlO signal, we concluded that the inelastic collisions have negligible effect.

B. Rotational distribution for $AI({}^{2}P_{1/2})$ and $AI({}^{2}P_{3/2})$ and the reaction mechanism

The rotational distributions discussed above were those for the reaction products from the mixed reactants, $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$. The interaction potentials for these two states have been suggested to be different,¹⁹ and the product state distribution for each state is expected to provide more detailed information about the reaction mechanism. The results are summarized in the following:

- (1) The rotational distributions are quite similar to each other for $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$ at two different collision energies, 12.2 kJ/mol and 18.4 kJ/mol;
- (2) The relative reactivity of the two components depends on the collision energy. At lower collision energy, 12.2 kJ/mol, $Al({}^{2}P_{1/2})$ is about three times more reactive than $Al({}^{2}P_{3/2})$, while their reactivities are comparable at a collision energy of 18.5 kJ/mol.

The second result is consistent with the observation by Naulin and Costes.¹⁷ They determined the relative cross sections for two components by measuring band heads of the AlO transition. They observed that $Al({}^{2}P_{1/2})$ is more reactive than $Al({}^{2}P_{3/2})$ at low collision energies while their cross sections become comparable each other at high collision energies. Our result again confirms that the excited spin–orbit state does react with O₂ but is less reactive at low collision energy. More importantly we observed that the rotational distributions for the two spin–orbit states are very similar at low and high collision energies. That is, at low collision energy, the difference between the two spin–orbit states appears only in their reactivity, and the rotational distribution does not depend on the initial spin–orbit state.

The different reactivity of the two spin-orbit states has been explained by the long-range interaction potential consisting of the quadrupole-quadrupole and the dispersion interactions.^{18,19} In the case of Al(${}^2P_{1/2}$), the reaction is controlled by dispersion forces, which are attractive and lead to barrierless reaction at any collision energy. On the other hand, the reaction of $Al({}^{2}P_{3/2})$ is dominated by the electrostatic quadrupole-quadrupole interaction at very low collision energy while it is controlled by dispersion forces at higher energy. For the quadrupole-quadrupole interaction, the potential depends on the orientation of the approach of Al to O₂, i.e., collinear approach leads to an entirely repulsive interaction for $Al({}^{2}P_{3/2})$ and this repulsive interaction is reduced by changing the orientation from collinear to bent. The lower reactivity of Al(${}^{2}P_{3/2}$) is ascribed to this steric factor in the interaction potential. Based on this model, it could be expected that the difference of the entrance channel between two spin-orbit states lead the difference in the product rotational state distribution. However, the results we observed show no substantial difference between the rotational distributions for $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$. One reasonable explanation is the occurrence of an intermediate complex in the course of reaction (1). This intermediate complex might be formed for $Al({}^{2}P_{1/2})$ for any orientation of approach while only a limited range of orientations can lead to the intermediate for $Al({}^{2}P_{3/2})$. Although the limited range orientations of reactive encounters for $Al({}^{2}P_{3/2})$ leads to lower reactivity, the system loses memory of the formation of the intermediate complex, and provides the same rotational distribution for both spin–orbit states of Al.

According to the long-range interaction model, the dispersion interaction becomes dominant for both $Al({}^{2}P_{1/2})$ and $Al({}^{2}P_{3/2})$ at high collision energy.^{18,19} The attractive interaction for both states leads to the intermediate complex and the reaction again loses memory of the initial state in the complex. Therefore, it is reasonable that both the rotational distribution and reactivity become similar for the two spin–orbit states at high collision energy.

The formation of the intermediate complex is consistent with the potential energy surface calculated recently by Pak and Gordon.²¹ According to their calculation, two doublet potential surfaces, ${}^{2}A_{1}$ and ${}^{2}A_{2}$, have global minima at a cyclic AlO₂ structure while no reaction path leading from Al+O₂ directly to AlO+O is located. From the viewpoint of energy randomization, formation of the intermediate complex may not be consistent with the energy partitioning we observed. If the energy randomizes completely within the complex, the energy partitioning is expected to be statistical. Our results showed a little deviation from statistical energy partitioning, and it might suggest the existence of an exit channel interaction between departing products or short lifetimes of the complex.

V. SUMMARY

The reaction of Al with O2 was studied by using a crossed-beam technique at five collision energies. The rotational and vibrational distributions of the product AlO were determined from the LIF spectra of the AlO($B^{2}\Sigma^{+} - X^{2}\Sigma^{+}$) transition. The energy partitioning into the rotation and vibration of AlO was observed to be a little lower than that expected from the statistical model. The rotational state distributions of AlO were determined for the first time for two spin-orbit components of Al, Al(${}^{2}P_{1/2}$) and Al(${}^{2}P_{3/2}$). The relative reactivity of these components was different at low collision energy, however their product rotational distributions were observed to be almost identical. Their reactivities and rotational distributions became similar at higher collision energy. These results suggest that the reaction proceeds via an intermediate complex in which the initial condition such as an orientation of approach is lost and the available energy randomizes almost completely.

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APPENDIX: THE LIF INTENSITY FOR PARTIALLY SATURATED ABSORPTION

In the two-level model consisting of lower level 1 and upper level 2, the rate equation for the population of the level 2, N_2 , is given by the equation,

$$\frac{dN_2}{dt} = B_{12}\rho N_1 - (B_{21}\rho + A_{21})N_2, \qquad (A1)$$

where N_1 , N_2 , ρ , B_{12} , B_{21} , and A_{21} are the populations of levels 1 and 2, the density of radiation, the integrated Einstein coefficients for absorption, stimulated emission, and spontaneous emission, respectively. In the transition from the level of rotational quantum number, J_i to J_j , B_{ij} is expressed by the Hönl–London factor, S_{ij} , as

$$B_{ij} = \frac{kS_{ij}}{2J_i + 1} = \frac{kS_{ij}}{g_i}.$$
 (A2)

Here, g_i is the degeneracy of the J_i level and $k = 2\pi^2 R^2/3\epsilon_0 h^2$ (*R* is the vibrational and electronic part of the transition moment, *h* is the Planck constant, ϵ_0 is the permittivity of vacuum).²⁶ Then the rate Eq. (A1) is given by

$$\frac{dN_2}{dt} = \frac{kS_{ij}}{g_i} \rho N_1 - \left(\frac{kS_{ji}}{g_j} \rho + A_{21}\right) N_2.$$
(A3)

By using the relation of $S_{ij}=S_{ji}$, and neglecting the contribution of spontaneous emission which is small compared to the stimulated emission under the saturation condition, the rate equation can be integrated for the rectangular pulse duration, Δt . The result under the condition of $N_2(t=0)=0$ is the following:

$$N_2 = N \frac{g_2}{g_1 + g_2} \left[1 - \exp\left(-\frac{g_1 + g_2}{g_1 g_2} S_{12} \rho k \Delta t \right) \right].$$
(A4)

Here, $N = N_1 + N_2$ is the population of the molecule initially prepared in the lower level. The LIF intensity is proportional to the population of the upper level, N_2 , then given by

$$I_{\rm LIF} = cN \frac{g_2}{g_1 + g_2} \bigg[1 - \exp\bigg(-\frac{g_1 + g_2}{g_1 g_2} S_{12} \rho k \Delta t \bigg) \bigg], \quad (A5)$$

where c is the proportionality constant determined by experimental conditions. In the two extreme cases, the absorption is fully saturated or depends linearly on the radiation density, and the equation is reduced to the following equations, respectively:

$$I_{\rm LIF} = cN \frac{g_2}{g_1 + g_2},\tag{A6}$$

$$I_{\rm LIF} = c \, \frac{NS_{12}\rho k\Delta t}{g_1}.\tag{A7}$$

In the intermediate case, the dependence of the LIF intensity may be approximated as ρ^n , where *n* changes from 0 to 1. This corresponds to the replacement of the factor $[1 - \exp\{-(g_1 + g_2)S_{12}\rho k\Delta t/g_1g_2\}]$ by $\{(g_1 + g_2)S_{12}\rho k\Delta t/g_1g_2\}^n$, then I_{LIF} is given by

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$$I_{\rm LIF} = cN \frac{g_2}{g_1 + g_2} \left(\frac{g_1 + g_2}{g_1 g_2} S_{12} \rho k \Delta t \right)^n$$
$$= c \frac{N}{g_1} \left(\frac{g_1 g_2}{g_1 + g_2} \right)^{1-n} (S_{12} \rho k \Delta t)^n.$$
(A8)

For the $B^2\Sigma - X^2\Sigma$ transition of AlO, S_{12} for *P* and *R*-branches are approximated by J'' and J'' + 1, respectively. Then Eqs. (A6)–(A8) are given for the *P*-branch in the following:

$$I_{\rm LIF} = c \, \frac{N}{g_1} \frac{g_1 g_2}{g_1 + g_2} = c \, \frac{N}{g_1} \frac{(2J'' + 1)(2J'' - 1)}{4J''} \approx c \, \frac{J''N}{g_1}, \tag{A9}$$

$$I_{\rm LIF} = c \, \frac{J''N}{g_1} \rho k \Delta t, \tag{A10}$$

$$I_{\rm LIF} = c \, \frac{N}{g_1} \left(\frac{(2J''+1)(2J''-1)}{4J''} \right)^{1-n} (J''\rho k\Delta t)^n$$
$$\approx c \, \frac{N}{g_1} (J'')^{1-n} (J''\rho k\Delta t)^n = c \, \frac{J''N}{g_1} (\rho k\Delta t)^n.$$
(A11)

Since the electronic and vibrational transition moment and the pulse width of the laser are constant, the LIF intensity for the *P*-branch is given by Eq. (A12),

$$I_{\rm LIF} = C_0 \frac{J''N}{g_1} \rho^n, \tag{A12}$$

where $C_0 = c(k\Delta t)^n$. A similar derivation is applied for the LIF transition of the *R*-branch and the LIF intensity is given by Eq. (A13),

$$I_{\rm LIF} = C_0 \frac{(J''+1)N}{g_1} \rho^n.$$
(A13)

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