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Detection of O(^3P_J) atoms formed by reaction, Al+O$_2$→ AlO+O under crossed-beam condition

Masayuki Ishida, Tomohiko Higashiyama, Yoshiteru Matsumoto, and Kenji Honma[a)]
Department of Material Science, University of Hyogo, 3-2-1 Kohto, Kamigori, Hyogo 678-1297, Japan

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The vacuum ultraviolet laser-induced fluorescence technique was employed to detect the oxygen atoms formed by the reaction, Al+O$_2$→ AlO+O. The measurements were carried out under the crossed-beam condition at 12.2 kJ/mol of collision energy. The relative populations of three spin-orbit states of O(^3P_J) were determined to be 3.8, 1.0, and 0.2 for J=2, 1, and 0, respectively. They show nonstatistical populations, i.e., more population in O($^3P_2$) and less population in O($^3P_0$) than the statistical expectation. These populations were almost identical for two Al beam conditions where the relative concentrations of two spin-orbit states of Al, $^2P_{1/2}$, and $^2P_{3/2}$, are different. These results suggest that the reaction of Al with O$_2$ proceeds via an intermediate complex where the memory of the initial spin-orbit state is lost. Deviation from the statistical population of O(^3P_J) implies the occurrence of the interaction among potential surfaces in the exit channel. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1924387]

I. INTRODUCTION

Effects of electronic excitation on chemical reactions have been one of the important issues in reaction dynamics. They are especially important for reactions of transition-metal atoms which usually have several low-lying electronically excited states.[1–5] In the electronic excitation, spin-orbit states have unique properties from both dynamical and kinetical points of view. Atoms with both nonzero electronic angular momentum and spin multiplicity have spin-orbit fine structure and the spin-orbit effects, which describe the differences in reactivity of individual levels of different total angular momentum, J, are sometime significant even in the cases of small fine-structure splittings.[6–9] The effects of spin-orbit fine structures on reactivities have special importance for reaction kinetics, since the energy differences of the spin-orbit levels in many atoms are small compared with thermal energy and excited states have significant populations and contributions to thermal rate constants.

One of the metal-atom reaction systems in which the spin-orbit effects have been studied is the reaction,[10]

$$\mathrm{Al}(^2P_{1/2,3/2}) + \mathrm{O}_2(X\,^3\Sigma_g^-) \rightarrow \mathrm{AlO}(X\,^2\Sigma^+) + \mathrm{O}(^3P_J) \qquad \Delta_r H_0^0 = -14.96\ \mathrm{kJ/mol} \qquad (1)$$

The ground-state electron configuration of the Al atom forms two spin-orbit states, Al($^2P_{1/2}$) and Al($^2P_{3/2}$), whose splitting is rather small, 112.04 cm^{-1}; however, the effect is significant and depends on collision energy.[11–14] At low collision energies, the spin-orbit excited state, Al($^2P_{3/2}$), is less reactive with O$_2$ than the ground state, Al($^2P_{1/2}$). The relative cross section of Al($^2P_{3/2}$) increases with the collision energy and becomes comparable to that of Al($^2P_{1/2}$). Recently, we studied reaction (1) by using the crossed-beam laser-induced fluorescence technique and determined the rotational and vibrational distributions of AlO for each spin-orbit state.[15] While our results again confirmed the lower reactivity of the excited state, Al($^2P_{3/2}$), the rotational and vibrational distributions of AlO corresponding to two spin-orbit levels were quite similar to each other. These results, different reactivities and similar energy partition, suggest that reaction (1) proceeds via intermediate complexes which are supported by recent theoretical study.[16] Because both spin-orbit states lead to the intermediate complexes, AlO$_2$, in which the energy randomizes, the rotational and vibrational state distributions become similar for both reactant states.

In the present study, we wish to present experimental results for the other half of the products of reaction (1), i.e., the oxygen atom. The O atom was detected by vacuum ultraviolet laser-induced fluorescence (LIF) and the relative populations of its spin-orbit states, O(^3P_J) (J=2,1,0), were determined at 12.2 kJ/mol of collision energy. The Doppler line profiles of the LIF transitions were also analyzed to obtain energy partitioning into the products of reaction (1). Combined with the previous study, more detail information was derived for the potential energy surfaces and the mechanism of reaction (1).

II. EXPERIMENT

The experiment was carried out by using a crossed-beam apparatus described in the previous paper.[15] Briefly, the apparatus consisted of three chambers which were differentially pumped. Al atoms were generated by laser vaporization. The fourth harmonic of an yttrium aluminum garnet (YAG) laser (Spectra Physics GCR-150-10) was focused onto an Al rod (99.999% purity, Goodfellow Cambridge Limited) which was rotated and translated by a stepping motor. The vaporized Al atoms were cooled and issued as an atomic beam by carrier gas flow expanded through a pulsed valve (Jordan PSV, 1.0-mm diameter) A pure oxygen mo-

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[a)] Author to whom correspondence should be addressed; electronic mail: honma@sci.u-hyogo.ac.jp lecular beam was delivered from another pulsed valve (an Even–Lavie valve, 0.2-mm diameter).[17] Both beams were collimated by skimmers (Beam Dynamics, 2-mm diameter) and crossed each other at a right angle in a reaction chamber. The metal-atomic beam source, the O_2 beam source, and the reaction chamber were pumped by 6-, 10-, 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 4×10^{-6} Torr, respectively.

In the present measurements, Ne and N_2 were used as the carrier gases for the Al atom. Both carrier gases provide the Al atomic beam of the same peak velocity with a similar width (±6%), 1045 m/s.[15] The unique properties of N_2 and Ne carrier gases are the relative populations of two spin-orbit states of Al, Al($^2P_{1/2}$), and Al($^2P_{3/2}$). The N_2 carrier provides mostly the ground spin-orbit state, Al($^2P_{1/2}$), while the Ne carrier provides both Al($^2P_{1/2}$) and Al($^2P_{3/2}$) with comparable concentrations.[12,15] Although the relative concentrations of the spin-orbit states were not determined prior to each measurement in this study, it could be stated from our previous measurements that the Al($^2P_{1/2}$) concentration in the beam is more than 80% for the N_2 carrier and 50% for the Ne carrier. Since the metal beam source has no extension channel, the concentration of Al clusters is believe to be negligible.

The velocity of the O_2 beam was measured by a fast ionization gauge (Beam Dynamics, FIG). The determined velocity was 760 m/s(±7%) and the collision energy was 12.2 kJ/mol. After the previous study, a quadrupole mass spectrometer (ULVAC, MSQ-150A) was installed on the O_2 beam axis. Since the Lavie–Even valve has been used to generate large clusters,[17] it has to be confirmed that the contribution of clusters is minor in this study. Under the experimental condition used here, no signal more than the noise level was observed at $m/z=64$, $(O_2)_2^+$. Although an electron-impact ionization may cause some fragmentation, this result suggests that the concentration of the O_2 dimer and larger clusters is negligible.[18]

The O atom was detected by the vacuum ultraviolet (VUV) LIF technique by using the transition, O($^3S_1^0$-^3P_J). The vacuum ultraviolet light was generated by the four-wave difference frequency mixing in Kr. Two dye lasers (Continuum ND-6000 and ND-60 using DCM as a dye in both lasers) were pumped by a Nd:YAG laser (Continuum NY-82). The frequency of one dye laser was tripled by KD*P and beta barium borate (BBO) crystals and tuned with the two-photon transition to one of the excited states of Kr, $5p[5/2,2]$. This UV laser beam, 46 154.1 cm^{-1} (around 217 nm), and the output of the other dye laser were propagated coaxially and focused into a conversion cell by a quarts lens ($f=200$ mm). The conversion cell containing Kr was located in the center of the reaction chamber and the propagation axis of the laser beams was perpendicular to the axes of atomic and molecular beams. A MgF_2 plate was used for the output window of the Kr cell. No device was used to separate the VUV laser light from the UV and visible ones, then all laser lights were irradiated on the two-beam crossing region.

The VUV fluorescence from the crossing region was collected by a MgF_2 lens ($f=50$ mm) and detected by a VUV solar blind photomultiplier tube (EMR 541G-08-17). The output of the photomultiplier tube was amplified by a preamplifier (SRS SR-445) and fed into a gated integrator (SRS SR-250). The excitation VUV laser intensity was measured by a Ceratron electron multiplier located near the outlet Brewster window of the reaction chamber and its signal was amplified and averaged by another gated integrator. The averaged signals of the fluorescence and laser intensity were stored in a computer for further analysis.

As described in the previous paper, the Al beam contains a trace amount of AlO. We also observed the LIF signal of the O atom even without the O_2 molecular beam crossing with the Al beam. As discussed in Sec. III, this LIF signal originates from the O atom formed at the laser vaporization region. In order to eliminate the contribution of the O atom in the Al beam, the O_2 beam was operated with 5 Hz while the Al beam was operated with 10 Hz, and the 5-Hz signal synchronized with O_2 beam and that synchronized without O_2 were averaged separately by two gated integrators and accumulated by a computer. The difference of the two signals was obtained by simple subtraction.

III. RESULTS AND DISCUSSION

A. O atom in Al beam

As mentioned in the Experiment section, the LIF signal of the O atom was observed without the O_2 beam. One possible origin is the O atom generated in the laser vaporization region, i.e., the O atom formed by the dissociative desorption of oxidized surface of the Al rod and/or by the reactions of the vaporized Al with trace of oxidant in the carrier gas. Another possibility is the photolysis of AlO in the Al beam at the crossing region. Since the bond dissociation energy of AlO is 5.27 eV,[12] the small amount of AlO in the Al beam could be photolyzed by the UV (46 154.1 cm^{-1} corresponding to 5.72 eV) and/or VUV laser lights. If the second process occurs with a certain extent, the photodissociation of the AlO formed by reaction (1) should be also taken into account.

Figure 1 shows the O($^3S_1^0$-$^3P_2$) LIF intensity as a function of the VUV laser intensity. In this measurement, the intensity of the VUV laser was changed by various manners, i.e., changing UV and/or visible laser intensities, and the pressure of Kr in the conversion cell. Although the data taken by using the UV and visible lasers of various intensities are shown in one plot, the LIF intensity seems to depend linearly on the VUV laser intensity. The UV laser intensity shows no effect on the LIF intensity of the O atom. This result strongly suggests that the photodissociation of AlO by the UV laser (46 154.1 cm^{-1}) is negligible in this experimental condition and the O atom observed in the Al beam originated at the laser vaporization region. The linear dependence shown in this figure also confirms that the O($^3S_1^0$-^3P_J) transition is not saturated for the VUV laser intensity used in this study.

The above conclusion is supported by the relative populations of the spin-orbit states of O(^3P_J) in the Al beam. We observed that O($^3P_2$) had a much larger population com-

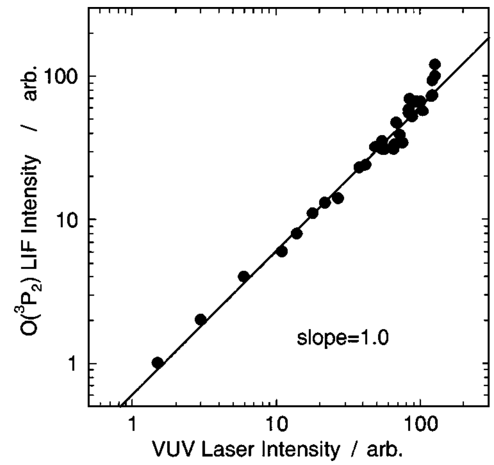

FIG. 1. VUV laser intensity dependence of LIF intensity of O($^3P_2$) in Al beam.

pared with the other two states, as summarized in Table I. The observed high population of the lowest-energy spin-orbit states can be explained by the supersonic expansion following to the O atom formation. The O atoms formed at the laser vaporization region are cooled by many collisions with carrier gas molecules.

B. Populations of O(^3P_J) formed by reaction (1)

The LIF spectra of the O atom formed by reaction reaction (1) were obtained by eliminating the contribution of the O atom in the Al beam. The Al and O$_2$ beams were operated with 10 and 5 Hz, respectively. The 5-Hz signal synchronized with the O$_2$ beam and that synchronized without O$_2$ was averaged separately by two gated integrators and accumulated by a computer. The difference of the two signals was obtained by simple subtraction. The difference was then divided by the VUV laser intensity to obtain the normalized LIF intensity, since the absorption of O($^3S_1^0$-^3P_J) depends linearly on the VUV laser intensity, as shown in Fig. 1. The LIF spectra were measured several times and averaged. Figure 2 shows the averaged spectra for the N$_2$ carrier gas.

Each spectrum was fitted by the Gaussian function to obtain an area of the absorption line. In this figure, the best fits are shown as broken lines. Since the transitions used here have a common upper state, O($^3S_1^0$), and the absorption line strengths for three O(^3P_J) states are almost identical,[19] no further correction was necessary to determine the populations of three states. The results of relative populations are summarized in Table I and Fig. 3. Those determined for the Al beam of the Ne carrier were also shown in this table. Because the populations of the highest-energy O($^3P_0$) have the largest errors, all relative populations are given with respect to those of O($^3P_1$).

TABLE I. Relative populations of spin-orbit states of O(^3P_J) formed by reaction (1).

	$J=2$	$J=1$	$J=0$
Population of O(^3P_J)			
Al/N$_2$	3.9±1.0	1.0±0.1	0.2±0.1
Al/Ne	3.8±0.8	1.0±0.2	[a]
Statistical expectation	1.95	1.00	0.31
in Al/N$_2$ beam	23±10	1.0±0.3	0.4±0.1

[a] Because of poor signal-to-noise ratio, reliable measurement could not be accomplished.

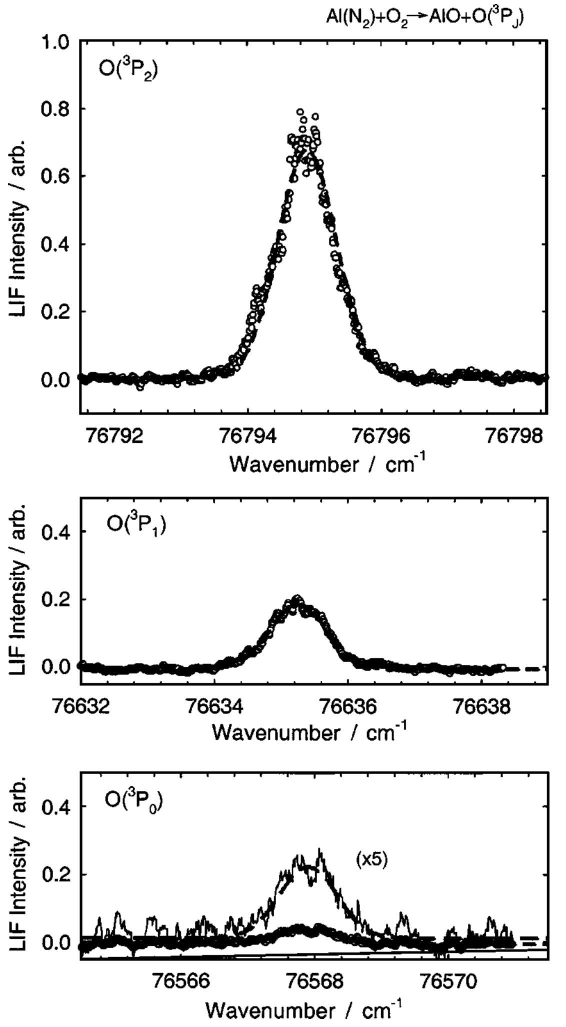

FIG. 2. LIF spectra of O(^3P_J) (J=0,1,2) formed by the reaction of Al +O$_2$. The broken lines are Gaussian fits for the spectra.

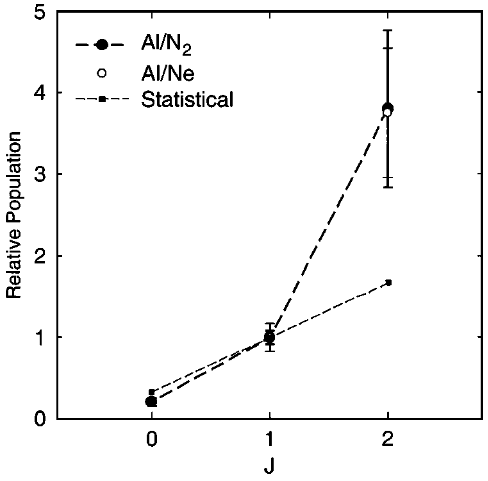

FIG. 3. Relative populations of O(^3P_J) (J=0,1,2) formed by the reaction of Al+O$_2$. The open circles and solid circles are those for the Al beams of N$_2$ carrier and Ne carrier, respectively. Also shown by solid squares are the population expected from statistical energy partitioning into products.

Compared with the Al beam of the N_2 carrier, that of the Ne carrier contains more spin-orbit excited state, $\mathrm{Al}(^2P_{3/2})$. Because this state is less reactive with O_2 than the ground state, $\mathrm{Al}(^2P_{1/2})$, the O atom signal for the Al beam of the Ne carrier was significantly weaker and reliable population for $\mathrm{O}(^3P_0)$ could not be determined. Except for $\mathrm{O}(^3P_0)$, the populations determined for two carrier gases agree very well. These results suggest that two spin-orbit states of Al provide no significant effect on the spin-orbit state populations of the product O atom.

The determined populations could be compared with those expected from statistical energy partitioning in the products, AlO+O. The statistical populations of the spin-orbit states of $\mathrm{O}(^3P_J)$ were estimated by

$$N^0(J) \propto (2J+1)\sum_{v}\sum_{N}(2N+1)(E_{\mathrm{av}}-E_v-E_r-E_{\mathrm{so}})^{1/2}$$
$$\propto (2J+1)\sum_{v}\sum_{N}N^0(v,N),$$

where E_{av}, E_v, E_r, N, and E_{so} are total available energy of the reaction, vibrational energy of AlO, its rotational energy, rotational quantum number, and spin-orbit energy of the O atom, respectively. $N^0(v,N)$'s are the statistical distribution of AlO with vibrational and rotational quantum numbers, v and N, respectively. The estimated values were 1.95:1.00:0.31 for $J=2:J=1:J=0$, respectively. The present results show that reaction (1) forms more ground spin-orbit state, $\mathrm{O}(^3P_2)$, and less excited state than the statistical expectation, i.e., the observed populations deviate significantly from the statistical ones.

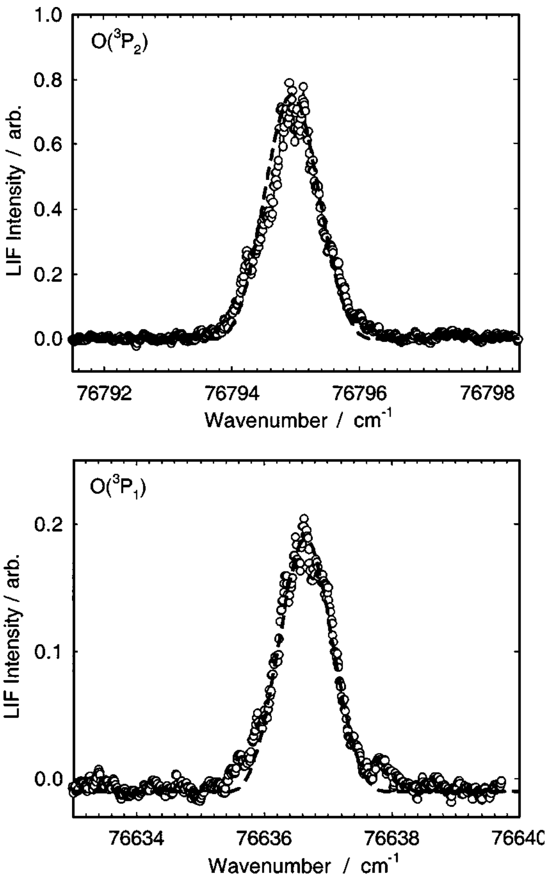

FIG. 4. LIF spectra of $\mathrm{O}(^3P_J)$ $(J=1,2)$ formed by the reaction of Al with O_2. Also shown by broken lines are convoluted spectra based on the statistical energy partitioning and linewidths of VUV laser.

C. Analysis of LIF line shape

Generally, the Doppler line shapes of the O atom transitions contain some information about recoil energy in reaction (1). Because the reaction has only three atoms, the recoil translational energy directly correlates to the rotational and vibrational energy partitioning into the counterproduct AlO, which have been reported to be almost statistical at low collision energies.[12,15,20] The line shapes expected from the statistical energy partitioning were convoluted and compared with the observed ones.

The distributions of the vibrational and rotational states of AlO expected from statistical energy partitioning were estimated by $N^0(v,N)\propto(2N+1)(E_{\mathrm{av}}-E_v-E_r-E_{\mathrm{so}})^{1/2}$, as described in Sec. III B. The recoil energy, $E_{\mathrm{av}}-E_v-E_r-E_{\mathrm{so}}$, was converted to the recoil velocity and the Doppler shift of the O atom absorption. Since the propagation axis of the VUV laser is perpendicular to the scattering plane defined by atomic and molecular beams, the conversion of the center-of-mass (c.m.) recoil energy to the velocity component along the laser propagation axis is straightforward. Since no information about the differential cross section of reaction (1) is available, an isotropic c.m. angular distribution was assumed for the convolution of the Doppler profile.

The linewidths of the O atom transitions observed in the Al beam were used for the linewidths of the VUV laser. These O atoms formed in the source region are cooled by the supersonic expansion and expected to have narrow velocity components along the VUV laser propagation axis. As mentioned in Sec. III B, the O atom in the Al beam consists of mostly the ground spin-orbit state, $\mathrm{O}(^3P_2)$; the $\mathrm{O}(^3S_1^0\text{-}^3P_2)$ transition was measured and fitted by the Gaussian function to determine the linewidth. The averaged linewidth was $0.93\pm0.12\ \mathrm{cm}^{-1}$ [full width at half maximum (FWHM)].

The convoluted spectra are shown as broken lines with the observed spectra in Fig. 4. Because the expected Doppler shifts of the O atom are small, the line shapes are mostly determined by the laser linewidth and insensitive to recoil angular distribution. The convoluted line shapes represent the observed ones reasonably well and these suggest that the line shapes of the O atoms are consistent with the energy partitioning of reaction (1) reported previously.

D. Reaction mechanism

The results observed in this study are summarized as the following:

(A) The populations of the spin-orbit states, $\mathrm{O}(^3P_J)$, show significant deviation from the statistical expectation.

(B) These populations do not show the dependence on the spin-orbit states of reactant, $\mathrm{Al}(^2P_{1/2,3/2})$.

The dynamics of reaction (1) has been studied by measuring the rotational and vibrational distributions of AlO. Most studies have consistently reported that the rotational and vibrational distributions of AlO are almost statistical and suggested a mechanism forming a long-lived intermediate complex.[11,12,20–22] Recently, we determined the rotational and vibrational distributions for the specific spin-orbit state, Al($^2P_{1/2}$) or Al($^2P_{3/2}$), and observed that the rotational distributions were quite similar to each other.[15] The different reactivities and the similar rotational distributions of AlO were explained by the formation of an intermediate complex in the course of reaction (1). At low collision energies, it has been suggested that the long-range interaction potentials between two spin-orbit states and O$_2$ are different, i.e., electrostatic quadrupole-quadrupole interaction for Al($^2P_{3/2}$) and dispersion force for Al($^2P_{1/2}$).[13,14] Because the quadrupole-quadrupole interaction depends on the orientation of the approach of Al to O$_2$, Al($^2P_{3/2}$) could form the intermediate only at a limited range of orientations while Al($^2P_{1/2}$) forms the intermediate complex at any orientation of approach. Although the steric factor for Al($^2P_{3/2}$) leads to lower reactivity, the system loses memory of the initial spin-orbit states in the intermediate complex, and provides the same rotational distribution for both spin-orbit states of Al. The complex formation for both spin-orbit states of Al may be consistent with one of the results observed in this study, i.e., no difference in the population of O(^3P_J) was observed for two spin-orbit states, Al($^2P_{1/2,3/2}$). However, the deviation from the statistical populations needs further consideration about mechanism.

Recent theoretical study by Pak and Gordon[16] has provided useful information about the mechanism of reaction (1). They studied the lowest two doublet potential surfaces. Both surfaces, $^2A_2$ and $^2A_1$ in C_{2v} symmetry, have deep potential wells. They also observed that there is no direct pathway from Al+O$_2$ to AlO+O. These results strongly suggest that reaction (1) proceeds via the intermediate complex, AlO$_2$. Since the surface leading to the $^2A_1$ intermediate has an energy barrier of around 20 kcal/mol, the reaction is likely to proceed via the $^2A_2$ intermediate in the collision energy studied here. From the intermediate to the product, AlO($^2\Sigma^+$)+O(^3P_J), the $^2A_2$ intermediate which belongs to the A'' symmetry in C_s group needs the crossing to the A' surface.

The formation of the intermediate complex might imply that the populations of the spin-orbit states of product, O(^3P_J), become statistical as observed for rotational and vibrational states. However, the results observed in this study show significant deviation from the statistical expectation. Unfortunately, the study by Pak and Gordon does not include the spin-orbit interaction, then no information can be derived about the mixing of the initial spin-orbit states, Al($^2P_{1/2,3/2}$), and the branching to the final spin-orbit states, O(^3P_J). One simple way to derive this information is to consider the correlation among reactants, intermediates, and products based on the extended point group.[23] For the reactants and intermediates, the C_{2v} symmetry group can be applied. In this symmetry group, both Al($^2P_{1/2}$)+O$_2$($X\ ^3\Sigma_g^-$) and Al($^2P_{3/2}$)+O$_2$($X\ ^3\Sigma_g^-$) belong to the $E_{1/2}$ symmetry. Since both intermediates, $^2A_2$ and $^2A_1$, also belong to the $E_{1/2}$ symmetry, the lowest two reactant states correlate to these intermediates. However, this correlation scheme indicates that only one of the degenerated states of Al($^2P_{1/2}$)+O$_2$($X\ ^3\Sigma_g^-$) can adiabatically correlate with the $^2A_2$ intermediate which is energetically accessible in the collision energy of 12.2 kJ/mol. Since most of the experimental results have suggested the formation of intermediate complexes for both spin-orbit states, there must be an interaction between a potential surface evolving from Al($^2P_{3/2}$)+O$_2$($X\ ^3\Sigma_g^-$) and the surface connecting Al($^2P_{1/2}$)+O$_2$($X\ ^3\Sigma_g^-$) and the $^2A_2$ intermediate.

More important for the branching of O(^3P_J) is the correlation between the intermediates and products. As Pak and Gordon indicate, the symmetry changes from C_{2v} to $C_{\infty v}$; it is reasonable to use the C_s symmetry group to connect them. In the C_s symmetry group, two intermediates and AlO($X\ ^2\Sigma^+$)+O(^3P_J) belong to the same $E_{1/2}$ symmetry. Since the $^2A_2$ ($^2A''$ in C_s symmetry group) intermediate and the lowest-energy AlO($X\ ^2\Sigma^+$)+O($^3P_2$) belong to the same symmetry, they may correlate adiabatically, while the surface crossing is necessary for the potential surfaces without taking into account the spin-orbit interaction. This adiabatic correlation is consistent with the high population of O($^3P_2$) observed in this study. On the other hand, an interaction with other potential surfaces is necessary for the O($^3P_{1,0}$) formation, since the potential surfaces for these products could not correlate with the intermediate $^2A_2$. Further discussion requires detail information about other electronic states at the intermediate region and the interaction among the surfaces from them and the $^2A_2$ intermediate.

IV. SUMMARY

The relative populations of three spin-orbit states, O(^3P_J), were determined for the reaction, Al+O$_2$→AlO+O, under crossed-beam condition. The measurements were achieved for two experimental conditions where the relative populations of two spin-orbit states of Al, Al($^2P_{1/2,3/2}$), are different. The observed relative populations were almost identical for two conditions and suggested the absence of the effect of the initial spin-orbit states. The lowest-energy O($^3P_2$) had the highest population which is twice as high as that expected from the statistical energy partitioning, while the highest-energy O($^3P_0$) populated less than the statistical expectation. Combined with the previous results, the results obtained in this study suggest that the reaction proceeds via the intermediate complex and the branching of the spin-orbit states is determined at the exit channel.

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