## Chemiluminescent reactions studied by laser ablation. Detection of AlO( $B^{2}\Sigma^{+}$ ) in the Al+O<sub>2</sub> system

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The chemiluminescent reaction between Al atoms produced by pulsed laser ablation and  $O_2$  molecules has been studied. The blue-green emission observed is assigned to the AlO B  $\rightarrow$ X transition. The vibrational distribution of AlO B state is describable as a Boltzmann distribution at 4500 ± 300 K. A mechanism for production of the AlO B state via an AlO<sub>3</sub> intermediate is proposed.

Chemiluminescent reactions of metal atoms in the gas phase have been an interesting topic for a long time. However, high boiling points of metals have been the limiting factor in these studies: only the reactions of metals with low boiling points such as Ca, Ba, Sr, etc., have been studied so far. Recently, laser ablation turned out to be a very simple and powerful technique to produce metal atoms or clusters in the gas phase. In this study we used laser ablation to generate Al atoms, and observed the chemiluminescence due to their reaction with  $O_2$  molecules.

A small cubic chamber  $(70 \times 70 \times 70 \text{ mm})$  was evacuated by a rotary pump  $(200 \ \text{g/min})$  to circa 1 mTorr (1 Torr=133.322 Pa). O<sub>2</sub> gas (Takachiho, 99.95%) was passed slowly through the chamber. The pressure of O<sub>2</sub> gas was monitored by a Pirani gauge. A small piece of Al substrate (Japan Lamp Industries, 99.999%) was set in the vacuum chamber. It was rotated with a small motor during the measurement so that a new surface of the substrate was ablated for each laser shot. The frequency-doubled output of an Nd<sup>3+</sup>: YAG laser (Quanta-Ray, DCR-2, 532 nm, circa 50 mJ, 10 Hz) was softly focused on the substrate by a quartz lens (f=20 cm). The diameter of the laser spot on the Al substrate was

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circa 1 mm. Chemiluminescence due to the reaction of ablated Al atoms with  $O_2$  molecules was collected by a quartz lens and detected by a photomultiplier tube (Hamamatsu photonics, R928) through a monochromator (Jasco, CT-80D or Nikon, G-250) blazed at 500 nm. A cylindrical wall (5 mm in height) on the substrate was effective to shield the observing zone from the strong emission of the plume. The signal from the photomultiplier tube was fed into a boxcar integrator (NF circuit, BX-530).

An intense blue-green emission of the AlO  $B \rightarrow X$ transition was observed in addition to emissions of Al atoms and ions generated by laser ablation. Although a weak UV emission due to the AlO  $C \rightarrow X$ transition was also observed, no emission of the AlO  $A \rightarrow X$  transition was detected. The observed  $\Delta v =$ v' - v'' = -1 sequence of the AlO  $B \rightarrow X$  transition is shown in fig. 1a. Since the relative intensities of vibrational bands of the  $\Delta v = -1$  sequence were independent of  $O_2$  pressure in the range of 0.1–0.5 Torr, vibrational relaxation of the AlO B state is thought to be negligible at pressures lower than 0.5 Torr. The intensity of the (0,0) band of the AlO  $B \rightarrow X$  transition showed a quadratic dependence on the  $O_2$ pressure.

Although some of the Al atoms ablated are in excited states, their contribution to the production of the AlO B state is probably negligible because almost all Al atoms are thought to relax to the ground state

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Fig. 1. (a) Observed  $\Delta \nu = -1$  sequence of the AlO  $B \rightarrow X$  transition of chemiluminescence spectrum. The pressure of  $O_2$  was 0.1 Torr. (b) Simulated spectrum with  $T_R = 2200$  K. (c) Simulated spectrum based on the phase space theory. The last state of  $O_2$  was assumed to be  $b^{\perp}\Sigma_s^{\perp}$ .

before they arrive in the observing zone (farther than 5 mm from the substrate).

Since the reaction

$$Al + O_2 \rightarrow AlO(X) + O \tag{1}$$

is almost isoenergetic, the AlO B state cannot be produced by a single collision between an Al atom and an  $O_2$  molecule. The probable mechanism for the production of the AlO B state is

$$Al + O_2 \rightarrow AlO(X) + O, \qquad (1)$$

$$AI + O + O_2 \rightarrow AIO(B) + O_2, \qquad (2)$$

which is consistent with the quadratic dependence of the emission intensity of the AlO  $B \rightarrow X$  transition on the O<sub>2</sub> pressure.

One might propose another mechanism:

$$AI + O_2 \rightarrow AIO(X) + O, \qquad (1)$$

$$0 + O_2 + O_2 \rightarrow O_3 + O_2$$
, (3)

$$AI + O_3 \rightarrow AIO(B) + O_2$$
. (4)

However, this mechanism can safely be eliminated for following reasons. First, this mechanism predicts a cubic dependence of the emission intensity of AlO  $B \rightarrow X$  on the O<sub>2</sub> pressure, while a quadratic dependence was observed experimentally. Second, no increase of AlO emission intensity due to the accumulation of O<sub>3</sub> molecule was observed.

The vibrational distribution of the AlO B state was determined by spectral simulation of the  $B \rightarrow X$  transition. The values of the molecular constants and Franck-Condon factors of AlO determined by Coxon and Naxakis [1] were used in the simulation. The rotational distribution was assumed to be a Boltzmann distribution. Parameters used for spectral simulation of the AlO  $B \rightarrow X$  transition were the rotational temperature and the relative vibrational population of the AlO B state. Fig. 1b shows a simulated spectrum of the  $\Delta v = -1$  sequence of the AlO  $B \rightarrow X$  transition. The rotational temperature was determined to be circa 2200 K. The vibrational distribution obtained is shown in fig. 2. The vibrational distribution of the AlO B state was found to be a Boltzmann distribution at 4200 K. Similarly, an analysis of the  $\Delta v = 1$  sequence of the AlO B  $\rightarrow$  X transition gave a rotational and vibrational temperature of 2000 and 4800 K, respectively. As an averaged



Fig. 2. Vibrational distribution of the AlO B state obtained by analysis of the  $\Delta v = -1$  sequence of the AlO B  $\rightarrow X$  transition.

value of both sequences, a rotational temperature of  $2100 \pm 100$  K and a vibrational temperature of  $4500 \pm 300$  K were obtained for the AlO B state.

The good fit to a Boltzmann distribution of the vibrational populations of the AlO B state suggests that the last step of AlO production is slow. If we assume an AlO<sub>3</sub> intermediate, step (2) can be rewritten as

$$Al+O+O_2 \rightarrow AlO_3, \qquad (2-1)$$

$$AlO_3 \rightarrow AlO(B) + O_2(X, a, b)$$
. (2-2)

We have applied phase space theory (PST) [2] to step (2-2) in order to predict the energy distribution of the AlO B state. The theory assumes that the distributions of reaction products among various states are governed only by state densities.

According to Zamir and Levine [2], the probability of finding two fragments in a particular quantum state is given by

$$P(v, j, V, J, E_{\mathrm{T}}) = g(j) g(J) \rho(E_{\mathrm{T}})$$
$$\times \delta(E^{*} - E_{\mathrm{T}} - E_{V} - E_{J} - E_{v} - E_{j}) / \rho(E^{*}),$$

where v, j are the vibrational and rotational quantum

numbers of one fragment, respectively, V, j are those of the other fragment,  $E_T$  is the relative translation energy, g is the degeneracy of a rotational level,  $\rho(E_T)$ is the density of translational states,  $\delta$  is a delta function, and  $E^+$  is the available energy.  $E_J$  can be treated as a continuous variable to a good approximation and a density  $\rho(E_J)$  can be introduced such that  $\rho(E_J) dE_J$  is the number of rotational states in the range  $E_J$ ,  $E_J + dE_J$ . In the case of dissociation of AlO<sub>3</sub> into two diatomic molecules, AlO(j, v) and O<sub>2</sub>(J, V),

$$g(j)=2j+1,$$

 $\rho(E_J) = \text{constant}$ ,

$$\rho(E_{\rm T}) = E_{\rm T}^{1/2}$$
.

Integrating over  $E_{T}$  and  $E_{J}$  gives the probability of finding AIO in the j and v state as follows:

$$P(v,j) \propto (2j+1) \sum \rho(E_{\nu}) (E^* - E_{\nu} - E_j - E_{\nu})^{3/2}$$
.

Fig. 1c shows a simulated spectrum based on PST assuming that the  $O_2$  molecule at step (2-2) is produced in the  $b^{1}\Sigma_{g}^{+}$  state. The envelope of the spectrum in fig. Ic reproduces well the experimental one (fig. 1a), although PST predicts a little less vibrational excitation and a little more rotational excitation than the experiment. The simulation with  $O_2$ a  ${}^{1}\Delta_{g}$  and X  ${}^{3}\Sigma_{g}^{-}$  states as the products of step (2-2) gave rotational excitation much higher than that observed. The simulated spectrum with the  $O_2 X {}^{3}\Sigma_{e}^{-1}$ state also showed highly vibrational excitation. We also simulated the AIO  $B \rightarrow X$  spectra based on the separate statistical ensembles (SSE) method [3] which is a modification of PST and was successfully applied to photodissociation of four-atom molecules such as NCNO [4]. The method gave results similar to PST: SSE predicts almost the same rotational energy distribution and a little higher vibrational energy distribution of the AlO B state than PST does. Therefore, it is expected that the AlO B state is produced mainly with the O<sub>2</sub> b  ${}^{1}\Sigma_{g}^{+}$  state at step (2-2). The large velocity of ablated Al atoms might affect the energy distribution of the AlO B state. However, we believe only slow Al atoms contribute to the production of the AIO B state because a large velocity of Al atoms is unfavorable for the three-body reaction.

The existence of AlO<sub>3</sub> is supported by a semiem-

pirical MO calculation. The MOPAC version 4.0 has been used for the MNDO UHF MO calculation. The optimized geometry of the AlO<sub>3</sub> ground state has a  $C_s$  symmetry and its energy level is circa 7200 cm<sup>-1</sup> lower than that of AlO(X)+O<sub>2</sub>(X). A matrix isolation experiment at 20 K [5] also suggests the existence of AlO<sub>3</sub>.

Comparison of this study with previous ones on chemiluminescence of AlO clarifies the advantages of the laser ablation technique. Reaction of a cw Al atom beam produced by using high temperature crucible with O<sub>2</sub> caused no [6] or only very weak structureless [7] emission. There has been no report of AlO  $B \rightarrow X$  emission for cw Al beam experiments under single- or multi-collision conditions to the author's knowledge. However, Jirvanov et al. [8] observed a strong emission from the AlO B state produced by a reaction between Al atoms and air at atmospheric pressure. They obtained Al atoms by the ruby laser vaporization technique. Frank and Krauss [9] observed time-resolved AIO  $B \rightarrow X$  emission by the high voltage discharge of O<sub>2</sub> gas between Al electrodes. The AlO  $B \rightarrow X$  spectra they obtained show much higher temperature than ours, probably because of heating of the  $O_2$  gas during the discharge.

High density of Al vapor produced by a pulsed laser ablation is crucial to observe the AlO  $B \rightarrow X$  emission

by the reaction  $Al+O+O_2$ . The vaporization rate of Al atoms under our experimental conditions was determined to be circa  $4 \times 10^{14}$  atoms/pulse based on the weight loss of the Al substrate. We estimated the pressure of Al atoms in the reaction zone to be of the order of 1 mTorr. This study demonstrates the usefulness of the laser ablation technique to investigate multi-collision reactions of metal atoms.

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