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Reactivities of spin-orbit states in Al(${}^{2}P_{1/2,3/2}$) + O₂(X ${}^{3}\Sigma_{g}^{-}$) \rightarrow AlO(X ${}^{2}\Sigma^{+}$) + O(${}^{3}P_{0,1,2}$). A fluorescence imaging study

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Abstract

A crossed beam chemical reaction, $Al({}^{2}P_{1/2,3/2}) + O_{2}(X {}^{3}\Sigma_{g}^{-}) \rightarrow AlO(X {}^{2}\Sigma^{+}) + O({}^{3}P_{0,1,2})$ was investigated by fluorescence imaging techniques. Multiplex detection of speeds and quantum states of both reactants and products has been implemented. The two spin-orbit states of Al atoms display distinctive reactivities towards O_{2} molecules. An electrostatic interaction model was employed to elucidate their dynamic behavior. A barrierless, attractive potential energy surface in the entrance valley of the allowed channel can be inferred from experimental results and model calculations.

1. Introduction

Fluorescence imaging techniques [1–3] have been demonstrated to be one of the multiplex detection methods in dynamic studies on chemical systems. Because chemical species are easily detected through either ion formation or laser-induced fluorescence (LIF), ion [4] and fluorescence imaging are complementary techniques. In this Letter, we report the first experimental result on a crossed beam chemical reaction, $Al({}^{2}P_{1/2,3/2}) + O_{2}(X {}^{3}\Sigma_{g}^{-}) \rightarrow AlO(X {}^{2}\Sigma^{+}) + O({}^{3}P_{0,1,2})$ by the fluorescence imaging techniques. Multiplex detection of speeds and spatial profiles of both reactants and products in specific quantum states has been implemented. We emphasize our findings on the reactivities of the two spin–orbit states of Al atoms towards O₂ molecules in the present report.

The chemical reaction $AI + O_2 \rightarrow AIO + O$ has been studied by Dagdigian, Zare, Costes and co-workers [5-7] in great detail. In our work, we employed the laser vaporization scheme [7-9] to generate the Al atomic beam. To detect reactants and products in a multiplex mode, the laser sheet illumination and two-dimensional imaging techniques (fluorescence imaging) [1-3] were utilized.

After a brief description of experimental procedures in Section 2, we present experimental image frames which can be analyzed to measure speeds of pulsed Al beams and reactivities of spin-orbit states. An

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electrostatic interaction model is proposed to examine the behavior of potential energy surface (PES) of $AI + O_2$ in the region of long-range interaction. The barrier height of the allowed channel of this reaction can be estimated from experimental results and model calculations.

2. Experiment

A schematic diagram of the experimental apparatus is depicted in Fig. 1. To execute studies on chemical reaction by the fluorescence imaging techniques, a crossed molecular beam machine has been constructed. The stainless steel apparatus had three differentially pumped compartments with two beam source chambers and an adjacent reaction chamber. Laser and view ports have been attached to various chambers at appropriate locations. All the chambers could be pumped down to 1×10^{-6} Torr without gas loads. After firing the beam valves, the pressure inside the reaction chamber was raised to $\approx 5 \times 10^{-5}$ Torr.

To generate pulsed Al beams, a laser vaporization scheme according to Smalley's design [8,9] was adopted. Photon pulses from a KrF excimer laser (Lambda Physik, EMG 53 MSC) at $\approx 10 \text{ mJ/pulse}$ were focused onto the target of an Al rod (Koch Chemicals, diameter 6 mm \times 50 mm, 99.999% purity) which was mounted inside the atomic beam source chamber. A pulsed beam valve (General Valve, IOTA ONE), which was positioned behind the metal target was fired at a specific time prior to fire KrF laser so as to confine and entrain the ablated plume. It was found that the arrangement without attaching an extension tube on the beam valve could generate the Al atomic beam with the shortest pulse duration. Inside the second source chamber, an identical beam valve was installed to generate pulsed O₂ molecular beams. To have a properly crossed beam configuration, both beam valves were mounted on the translational stages and the Gimbal mount to access precise alignment. To avoid deep crater formation on the Al rod by laser ablation, a driving mechanism was utilized to rotate and translate the metal target.

To detect Al atomic reactants and AlO radical products, two XeCl excimer laser pumped dye laser systems (Lambda Physik, LPX 200, LPD 3002E and COMPEX 200, SCANMATE 2E) were employed. They delivered tunable laser pulses around 395 (PBBO dyes) and 465 nm (coumarin 2 dyes) with a bandwidth ≈ 0.2 cm⁻¹ and pulse duration ≈ 15 ns. A 4.0 \times 0.1 cm² laser sheet with an effective length ≈ 10 cm was formed by passing the dye laser beam through a beam expander (Newport, T-27-25-300N) and a quartz cylindrical lens (focal length 50 cm). The central region of the laser sheet with a dimension of 2 cm which had a constant energy



Fig. 1. A schematic diagram of the experimental apparatus to study crossed beam chemical reactions of metal atoms by the fluorescence imaging techniques.

profile, was utilized to image Al or AlO. To enhance the signal-to-noise ratio, the energy of the dye laser pulses was kept at ≈ 1.5 mJ/pulse. An intensified charge-coupled device (CCD) (Princeton Instruments, ICCD-576G/RB) was installed to take image frames of fluorescing reactants and products from laser sheet illumination.

A precise timing sequence in triggering the two beam valves, the vaporization laser, the probe laser and the CCD camera was controlled by a four-channel delay generater (Stanford Research System, DG535). To carry out a fluorescence imaging experiment, detailed procedures have been described elsewhere [3] and will not be repeated here. We only emphasize that each subsystem should be tested independently and that an examination of the timing sequence beforehand is essential to any serious attempt in executing an imaging experiment.

3. Results and discussion

3.1. Speeds of pulsed Al atomic beams

In the absence of the O_2 molecular beam, time-resolved image frames of state-selected Al atomic bundles were obtained according to the experimental procedures described in Section 2. To measure the speed and spatial profiles of the two spin-orbit states of Al atomic reactants, the probe laser was tuned to induce atomic transition ${}^2S_{1/2} \leftarrow {}^2P_{1/2}$ (394.4 nm) or ${}^2S_{1/2} \leftarrow {}^2P_{3/2}$ (396.1 nm), where fluorescence from the 2S state was imaged by the CCD camera. Two representative image frames which display spatial profiles of Al atoms in the ${}^2P_{3/2}$ spin-orbit state at two different delay times with respect to the vaporization laser pulse are reproduced in Fig. 2. Without losing the spatial resolution, the electronic shutter of the CCD camera was opened 100 ns to cover several lifetimes ($\tau = 6.8$ ns [10]) of the 2S state of Al atoms. From the experimental image frames, the velocity distributions of Al bundles which have been entrained by various carrier gases can be measured. Our experimental results are summarized in Table 1 in conjunction with the velocity distribution of the O_2 molecular beam. Comparable results on laser-generated, pulsed Al atomic beams have been reported by Costes et al. [7], in which a fast ionization gauge was employed. As expected, we have found that the speeds of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ spin-orbit states were the same within experimental uncertainty. Further, the relative population of these two states has been estimated to be $N({}^2P_{1/2})/N({}^2P_{3/2}) = 2$, from the experimentally measured LIF intensities, the Einstein coefficients of the ${}^2S_{1/2} \leftarrow {}^2P_{1/2,3/2}$ transitions, laser energies and the degeneracy factors. Apparently, thermalization of the populations of the two electronic states by collisions between Al atoms and carrier gases is far from complete.

Our measurements are the first experimental realization of the spatial profiles of state-selected, atomic bundles of a metallic element by the fluorescence imaging techniques. Because the laser sheet intercepts the bundle horizontally, the three-dimensional distribution can be obtained by rotating the experimental image along its symmetry axis through 2π rad. Literally, a bundle of fast moving Al atoms with a shape of a bullet is generated by the laser vaporization scheme.

3.2. Reactivities of spin-orbit states

Under the crossed beam configuration, time-resolved image frames of state-selected Al atomic bundles were obtained according to similar procedures. Experimental results on the ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ spin-orbit states in the collision event between pulsed Al bundles and O₂ molecular beams are reproduced in column (a) of Figs. 3 and 4, respectively. Image frames of control experiments which register the spatial profiles of Al atomic bundles in the absence of the O₂ molecular beam are shown concurrently in column (b) of Figs. 3 and 4. To measure quantitatively the reactivities of the two spin-orbit states in a crossed beam chemical reaction with O₂ molecules, we plot the integrated intensities of Al atoms in ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ electronic states in the collision event with respect to the delay time in Fig. 5, relative to those from the control experiments. Evidently, Al



Fig. 2. Fluorescence images of laser-generated Al atomic beams in the ${}^{2}P_{3/2}$ spin-orbit state. Delay times with respect to the vaporization laser pulse are marked on the left margin. The wavelength of the probe laser was tuned to 396.1 nm. The dimension of each image frame is 5.6×3.4 cm². A color bar (false color) which codes the image intensity is shown below the image frames.

atoms in the ${}^{2}P_{1/2}$ spin-orbit state are reactive towards O_{2} molecules. On the other hand, Al atoms in the ${}^{2}P_{3/2}$ spin-orbit state undergo mostly inelastic collisions. As a matter of fact, backward scattered Al atoms in the ${}^{2}P_{3/2}$ state accumulate higher number density in the region of the probe laser sheet. The contribution from intercepted Newton spheres which originate from various scattering centers in the Al bundle probably accounts for our observation. A simulation study to analyze the inelastic collisions and resultant image frames is in

Table 1 Characteristics of velocity distributions of pulsed beams

Pulsed beam ^a	ν (m/s)	δν/ν (%)	Pulse duration (µs)	
Al/H ₂	3000	6.0	5	
Al/He	1720	6.4	10	
Al/Ar	640	8.6	15	
O ₂	750	7.3	≈ 300	

^a The stagnation pressure of carrier gases in pulsed Al beams was set at 6 bar.



Fig. 3. A temporal sequence of fluorescence image frames of Al reactants in the ${}^{2}P_{1/2}$ spin-orbit state under the condition of crossed beam chemical reaction with O₂ molecules (column (a)) and a control experiment in the absence of the O₂ molecular beam (column (b)). The wavelength of the probe laser was tuned to 394.4 nm. Delay times with respect to the vaporization laser pulse are marked on the left margin. The dimension and color codes of image frames are identical to those in Fig. 2.

progress. From Fig. 5, 10% Al atoms in the ${}^{2}P_{1/2}$ state are consumed at the end of the collision event. It is reasonable to infer that the crossed beam reaction between Al and O₂ in the present study is under a single collision condition.

Consequently, we have observed distinctive differences in reactivity for Al atoms in the two spin-orbit states, towards O_2 molecules. The ground state Al atoms in the ${}^2P_{1/2}$ level are reactive, while the excited state Al atoms in the ${}^2P_{3/2}$ level with an extra energy of 112 cm⁻¹ [7] are non-reactive. A thorough understanding of their dynamic behavior must rely on the knowledge of topographical features of PES of the Al + O_2 system. In the absence of such an ab initio calculation, a simple interaction model is examined instead.

3.3. Electrostatic interaction model and barrier height of $Al + O_2$ reaction

To rationalize the observed reactivities of Al atoms in the ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ spin-orbit states towards O_{2} molecules, we utilize an electrostatic interaction model [11-13] to study the splitting of these two energy levels. It is assumed that the two reactants approach each other in a C_{s} symmetry so that the only symmetry operation of the Al + O_{2} system is a reflection plane. The first non-null electrostatic interaction at a large separation of the two reactants (longer than the sum of the van der Waals radii) is the coupling between the electric quadrupole moment of an Al atom and the electric field gradient of an O_{2} molecule. An effective field which



Fig. 4. A similar sequence of fluorescence image frames of Al reactants in the ${}^{2}P_{3/2}$ spin-orbit state, with column (a) for reaction and column (b) for control.

has the proper symmetry property in the C_s point group and the appropriate tensor operators to couple the spin-orbit energy levels from a [Ne]3s²3p electronic configuration is given by

$$\mathscr{H}_{\rm eff} = B_0^2 Y_{20} + B_2^2 (Y_{22} + Y_{2-2}), \tag{1}$$



Fig. 5. A reactivity plot of the ${}^{2}P_{1/2}$ (\bullet) and ${}^{2}P_{3/2}$ (O) spin-orbit states of Al atoms towards O₂ molecules.

$$\mathscr{H} = B_0^2 Y_{20} + B_2^2 (Y_{22} + Y_{2-2}) + AL \cdot S,$$
⁽²⁾

where A is the spin-orbit coupling constant and is equal to 75 cm⁻¹ for a free Al atom.

From the theory of angular momentum [14], the basis functions which describe the two spin-orbit states are given by

$$|{}^{2}\mathbf{P}_{1/2,1/2}\rangle = -\left(\frac{1}{3}\right)^{1/2} |10\rangle \alpha + \left(\frac{2}{3}\right)^{1/2} |11\rangle \beta,$$
(3a)

$$|{}^{2}P_{1/2,-1/2}\rangle = \left(\frac{1}{3}\right)^{1/2} |10\rangle\beta - \left(\frac{2}{3}\right)^{1/2} |1-1\rangle\alpha,$$
(3b)

$${}^{2}\mathsf{P}_{3/2,3/2}\rangle = |11\rangle\alpha, \tag{3c}$$

$$|{}^{2}P_{3/2,1/2}\rangle = \left(\frac{2}{3}\right)^{1/2} |10\rangle\alpha + \left(\frac{1}{3}\right)^{1/2} |11\rangle\beta,$$
(3d)

$$|{}^{2}\mathbf{P}_{3/2,-1/2}\rangle = \left(\frac{2}{3}\right)^{1/2} |10\rangle\beta + \left(\frac{1}{3}\right)^{1/2} |1-1\rangle\alpha,$$
(3e)

$${}^{2}\mathsf{P}_{3/2-3/2} \rangle = |1 - 1\rangle\beta, \tag{3f}$$

where the ket vector $|1m\rangle$ is a spherical harmonics with l = 1; in addition, the spin functions α and β have their usual definitions.

From Eqs. (2) and (3), the energy matrix can be proven to be

$$\begin{vmatrix} {}^{2}\mathbf{P}_{1/2,1/2} \rangle & |^{2}\mathbf{P}_{3/2,-3/2} \rangle & |^{2}\mathbf{P}_{3/2,1/2} \rangle & |^{2}\mathbf{P}_{1/2,-1/2} \rangle & |^{2}\mathbf{P}_{3/2,3/2} \rangle & |^{2}\mathbf{P}_{3/2,-1/2} \rangle \\ \begin{pmatrix} -A & -2C & -2^{1/2}B & 0 & 0 & 0 \\ -2C & \frac{1}{2}A - B & -2^{1/2}C & 0 & 0 & 0 \\ -2^{1/2}B & -2^{1/2}C & \frac{1}{2}A + B & 0 & 0 & 0 \\ 0 & 0 & 0 & -A & 2C & 2^{1/2}B \\ 0 & 0 & 0 & 2C & \frac{1}{2}A - B & -2^{1/2}C \\ 0 & 0 & 0 & 2^{1/2}B & -2^{1/2}C & \frac{1}{2}A + B \end{pmatrix},$$

$$(4)$$

where $B = (20\pi)^{-1/2}B_0^2$ and $C = (20\pi)^{-1/2}B_2^2$. From the above matrix, it is clear that the two spin-orbit states split into three energy levels and each level is doubly degenerate in accordance with the Kramer's theorem [15]. The symmetry species of each energy level is $E_{1/2}$.

Before diagonalizing the 3×3 energy matrix, one should examine the behavior of energy levels of an Al atom in the region where the electrostatic interaction is stronger than the spin-orbit coupling term, so that the signs and the relative magnitudes of B and C can be estimated. In this limit, the orbital eigenfunctions of an Al atom are given by $2^{-1/2}(|11\rangle - |1 - 1\rangle)$, $2^{-1/2}(|11\rangle + |1 - 1\rangle)$ and $|10\rangle$, with their corresponding eigenvalues at $-B + 6^{1/2}C$, $-B - 6^{1/2}C$ and 2B. The $|10\rangle$ state of the Al atom eventually correlates with the ground state product AlO(X ${}^{2}\Sigma^{+}$), while the pair of states, $2^{-1/2}(|11\rangle - |1 - 1\rangle)$ and $2^{-1/2}(|11\rangle + |1 - 1\rangle)$, correlate with the excited state product AlO (A ${}^{2}\Pi$)¹. To maintain the order of energy levels in the correlation, the numerical value of B should be negative. In addition, $|C| \leq |B|$ in the limit of a small separation between the two reactants. Because the energy matrix is invariant with respect to the substitution $C \rightarrow -C$, their eigenvalues are symmetric with respect to C = 0.

¹ For a general account on spin-orbit effects in chemical reactions, see Ref. [16].

After diagonalizing the energy matrix in Eq. (4), unconventional PESs can be obtained by plotting their eigenvalues as functions of *B* and *C*. We have found that two repulsive and an attractive PESs originate from the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ spin-orbit states, respectively. The intersection of PESs in the Al + O₂ system is absent. According to the electrostatic interaction model, Al atoms in the ${}^{2}P_{3/2}$ state which experience repulsive PESs should be non-reactive, in accordance with our experimental findings. The PES which originates from the ${}^{2}P_{1/2}$ state is attractive and barrierless. Details of our numerical results will be published elsewhere.

The reported activation energy of the Al + O_2 reaction from an Arrhenius plot was given by -0.16 ± 0.08 kcal/mol [17]. The negative activation energy can be justified from our experimental findings on the reactivities of the two spin-orbit states. At equilibrium, Al atoms in the ${}^2P_{3/2}$ level which are non-reactive share a noticeable portion of the total population at high temperature. Thus, the reaction rate of the Al + O_2 reaction slows down in a high-temperature flow reactor when the temperature is raised higher.

Experimental studies on the AlO radical products by the fluorescence imaging techniques have been implemented. A complete account on the product measurements and the reaction dynamics of the $Al + O_2$ reaction will be published elsewhere.

4. Conclusions

A crossed beam chemical reaction has been studied by the fluorescence imaging techniques for the first time. In the Al(${}^{2}P_{1/2,3/2}$) + O₂(X ${}^{3}\Sigma_{g}^{-}$) \rightarrow AlO(X ${}^{2}\Sigma^{+}$) + O(${}^{3}P_{0,1,2}$) reaction, we have found that only the ground spin-orbit state, i.e. Al atoms in the ${}^{2}P_{1/2}$ level, are reactive towards O₂ molecules. An electrostatic interaction model is examined to reveal the dynamics in the region of large separation between the two reactants. It is shown that Al atoms in the ${}^{2}P_{3/2}$ spin-orbit state experience repulsive PESs and are non-reactive. In the entrance valley of the allowed channel, Al atoms in the ${}^{2}P_{1/2}$ spin-orbit state are governed by a barrierless, attractive PES.

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References

- [1] K. Chen, Chem. Phys. Letters 198 (1992) 288.
- [2] K. Chen and C. Pei, Chem. Phys. Letters 217 (1994) 471.
- [3] K. Chen, C. Kuo, M. Tzeng, M. Shian and S. Chung, Chem. Phys. Letters 221 (1994) 341.
- [4] D.W. Chandler and P.L. Houston, J. Chem. Phys. 87 (1987) 1445.
- [5] P.J. Dagdigian, H.W. Cruse and R.N. Zare, J. Chem. Phys. 62 (1975) 1824.
- [6] L. Pasternack and P.J. Dagdigian, J. Chem. Phys. 67 (1977) 3854.
- [7] M. Costes, C. Naulin, G. Dorthe, C. Vaucamps and G. Nouchi, Faraday Discussions Chem. Soc. 84 (1987) 75.
- [8] D.E. Powers, S.G. Hansen, M.E. Geusic, A.C. Pulu, J.B. Hopkins, T.G. Dietz, M.A. Duncan, P.R.R. Langridge-Smith and R.E. Smalley, J. Phys. Chem. 86 (1982) 2556.
- [9] J.B. Hopkins, P.R.R. Langridge-Smith, M.D. Morse and R.E. Smalley, J. Chem. Phys. 78 (1983) 1627.
- [10] J.Z. Klose, Phys. Rev. A 19 (1979) 678.
- [11] J.K. Knipp, Phys. Rev. 53 (1938) 734.
- [12] P.G. Barke, J.H. Tait and A. Dalgarno, Chem. Phys. Letters 1 (1967) 345.
- [13] P. Das, T. Venkitachalam and R. Bersohn, J. Chem. Phys. 80 (1984) 4859.
- [14] R.N. Zare, Angular momentum (Wiley, New York, 1988).
- [15] M. Tinkham, Group theory and quantum mechanics (McGraw-Hill, New York, 1964).
- [16] P.J. Dagdigian and M.L. Campbell, Chem. Rev. 87 (1987) 1.
- [17] N.L. Garland and H.H. Nelson, Chem. Phys. Letters 191 (1992) 269.