Photodissociation Dynamics of AlO at 193 nm using Time-Sliced Ion Velocity Imaging

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The photodissociation dynamics of AlO at 193 nm is studied using time-sliced ion velocity mapping. Two dissociation channels are found through the speed and angular distributions of aluminum ions: one is one-photon dissociation of the neutral AlO to generate Al(2P_u)+O(3P_g), and the other is two-photon ionization and then dissociation of AlO+ to generate Al+(1S_g)+O(3P_g). Each dissociation channel includes the contribution of AlO in the vibrational states \( v = 0 - 2 \). The anisotropy parameter of the neutral dissociation channel is more dependent on the vibration state of AlO than the ion dissociation channel.

Key words: Time-sliced ion velocity imaging, Photodissociation, AlO, Vibrational state, 193 nm

I. INTRODUCTION

The study of molecular photodissociation dynamics is important to understand the chemical changes of molecules along the potential energy surface, and is also helpful to obtain molecular photon absorption spectra and ionization detection schemes, especially resonance enhanced multiphoton ionization (REMPI) schemes. Over the past 50 years, theoretical [1–15] and experimental [16–23] studies have been conducted on the metal oxide AlO radicals that exist in large amounts in the cosmic space. Based on these previous studies, we have used (1+1) REMPI to detect AlO products through the intermediate state \( D^2\Sigma^+ \) near 244 nm when studying the oxidation reaction kinetics of aluminum atoms [20]. The main reason is that theoretically, the single photon energy at 244 nm is less than the dissociation energy of AlO, which was estimated as 42496 cm\(^{-1}\) [23], that is, at least at 238 nm, the AlO radical can dissociate.

The dissociation energy of AlO was determined by Hildenbrand [2] using mass spectrometry and Zare’s group [23] using laser-induced fluorescence as 41481 cm\(^{-1}\) and 42496 cm\(^{-1}\), respectively. The theoretical calculations gave the dissociation energy of AlO 41900 cm\(^{-1}\) [1], 42110 cm\(^{-1}\) [6] and 42993 cm\(^{-1}\) [15]. There are two main theoretical calculations showing the dissociation channels of several lower-energy electronic states of AlO, including the dissociation channels of \( X^2\Sigma^+, B^2\Sigma^+, A^2\Pi \), and \( C^2\Pi \) states in the energy increasing order [3, 15]. Among them, the \( X^2\Sigma^+ \), \( A^2\Pi \) and \( C^2\Pi \) states of AlO are associated with Al(2P_u)+O(3P_g), while the \( B^2\Sigma^+ \) state is associated with Al(2P_u)+O(1D_g). Hildenbrand [2] used mass spectrometry to obtain the dissociation energy of AlO\(^+\) cation about 12910 cm\(^{-1}\), which is almost 30000 cm\(^{-1}\) less than the value for the dissociation of neutral AlO. For the dissociation of AlO\(^+\) [3], the ground state \( X^1\Sigma^+ \) and the excited state \( A^1\Pi \) are correlated with Al\(^+(2P_u)+O(3P_g)\), while the bound \( a^3\Pi \) state and the repulsive \( b^3\Sigma^- \) state are correlated with Al\(^+(1S_g)+O(3P_g)\) [24, 25].

The above theoretical research needs experimental support to better understand the role of excited electronic states of AlO/AlO\(^+\) in the related dissociation dynamics. Here, our research on the dissociation of AlO at 193 nm will provide detailed measurements on the speed and angular distributions of the Al/Al\(^+\) products to understand the AlO dissociation dynamics in the assistance of theoretical calculations.

II. EXPERIMENTS

The crossed-beam setup we used with the time-sliced ion velocity imaging has been described previously [20, 26–28], and only one molecular beam is used in this experiment. Aluminum atoms are generated by laser ablation of the Al metal rod (97% Al, Alfa) at 532 nm, and then react with O\(_2\) injected by a pulse valve under a back pressure of about 12 atm. The formed AlO radicals fly into the main chamber after passing through a 3 mm skimmer (Beam Dynamics Model No.50) along...
the propagation direction of the molecular beam. The AlO beam intersects the 193 nm laser beam at a cross angle of 45°. The 193 nm beam is generated by an argon fluoride excimer laser (GAM Laser, Inc. EX5) with a operating frequency of 15 Hz. The polarization direction of the laser is parallel to the imaging plane of the detector. The laser has a pulse energy of about 1 mJ and is focused by a circular lens (f=35 cm). After the dissociation of AlO/AlO⁺, the ion lens projects Al⁺ ions to the detection system. The ion lens includes 23 circular electrode plates with a total operating voltage of 1800 V. The detector system contains two MCPs (75 mm, 60:1, 10 μm pore, 12 μm pitch, Photek), one phosphorscreen (P43, Photek) and a CCD camera (La Vision E-lite 1.4M). After using the event counting, the ion signal is accumulated to obtain the image.

III. RESULTS AND DISCUSSION

The velocity image of Al⁺ is obtained at 193 nm when O₂ is used as reaction gas and carrier gas, as shown in FIG. 1(a). A quarter of the enlarged image is shown in FIG. 1(b) and several rings are observed. The velocity of strong Al⁺ ions at and near the center is almost zero, which is due to the unreacted Al brought out by the carrier gas. The strongest ring has the slowest speed, the adjacent ring with a slightly faster speed is greatly reduced in strength, and the neighboring ring with a faster speed can only be seen faintly. We define these three rings as region A. The three outmost clear outer rings are defined as region B.

The Al⁺ speed distributions are derived by integrating the signal over θ=0°–360° and 0°±5°, respectively, as shown in FIG. 2 (a) and (b), where θ is the angle between the polarization direction of the photolysis laser and the recoil velocity of the products. Obviously, within a smaller angular range, the resolution of several peaks in the speed distribution is higher. The intensity of the slow three peaks is strongly decreased with the increase of speed, while the intensity of the fast three peaks is gradually decreased with the increase of speed. The speed distribution in FIG. 2(b) is converted to the total kinetic energy distribution of Al/Al⁺+O based on the conservation of recoil angular momentum, as shown in FIG. 3. The fit to the total kinetic energy release (TKER) spectra is shown in FIG. 3. According to the total kinetic energy distribution in FIG. 3, three peaks in region A are 9072 cm⁻¹, 10125 cm⁻¹ and 10960 cm⁻¹, respectively, and the energy gap between adjacent peaks is about 950 cm⁻¹, which is similar to the vibrational constant of AlO (X²Σ⁺, ωv=979 cm⁻¹) [29].

In the photodissociation of AlO+hv→Al+O, the conservation of energy gives:

\[ hv + E_{\text{int}}(\text{AlO}) - D_0(\text{AlO}) = E_{\text{trans}} + E_{\text{int}}(\text{Al}+\text{O}) \] (1)

where hv is the photon energy (here, hv=51813.5 cm⁻¹). \( E_{\text{int}}(\text{AlO}) \) and \( E_{\text{int}}(\text{Al}+\text{O}) \) are the internal energies of the AlO parent radical and Al⁺+O fragments, respectively. \( D_0(\text{AlO}) \) is the bond dissociation energy of AlO (42496 cm⁻¹) [23], and \( E_{\text{trans}} \) is the total kinetic energy release (TKER) into Al and O fragments. According to the energy conservation, the position of the different vibration levels of AlO(X²Σ⁺, v=0–2) is shown in the upper vertical line of FIG. 3. The available energy increases with the increase of vibrational level from 0 to 2. The ratio between the peak areas by fitting is AlO(v=1)/AlO(v=0)=0.17±0.03, and AlO(v=2)/AlO(v=0)=0.05±0.01, respectively. The AlO(v=0) state is dominant in the photodissociation dynamics of AlO radial at 193 nm in the molecular
beam condition. The TKER peak corresponding to AlO(v=0) obtained from the photodissociation of AlO gives $D_0$(AlO) of 42742±40 cm$^{-1}$, which is 245 cm$^{-1}$ higher than the value given by Zare’s group [23]. The difference of $D_0$(AlO) may be due to the rotational excitation of the AlO molecule by laser ablation. The full width at half maximum of the peak distribution at around 9072 cm$^{-1}$ in FIG. 3 is about 520 cm$^{-1}$, which indicates that due to the small rotational constant of AlO (B$_v$=0.6413 cm$^{-1}$), AlO may have a high rotational level N≈20 at the peak position.

The ionization energy of AlO is approximately 76624 cm$^{-1}$ [29]. Thus two-photon absorption at 193 nm (51813.5 cm$^{-1}$) can ionize AlO radical and due to the small dissociation energy of AlO$^+$, the newly formed AlO$^+$ can dissociate to Al$^+$+O, i.e., AlO+2$h\nu$→AlO$^+$+e, AlO$^+$→Al$^+$+$^3$S$_g$)+O($^3$P$_g$), or directly AlO+2$h\nu$→Al$^+$+$^3$S$_g$)+O($^3$P$_g$)+e. Thus, the conservation of energy gives
\[
2h\nu + E_{\text{int}}(\text{AlO}) - D_0(\text{AlO}^+) - IE = E_{\text{trans}} + E_{\text{int}}(\text{Al}^+ + \text{O}) + E_e \tag{2}
\]
where $D_0$(AlO$^+$) is the dissociation energy of AlO$^+$ (12910 cm$^{-1}$) [2] and $E_e$ is the kinetic energy of the electron. Three peaks in region B of FIG. 3 are about 11898 cm$^{-1}$, 12809 cm$^{-1}$ and 13800 cm$^{-1}$, respectively, and the energy gap between the peaks is about 950 cm$^{-1}$, which is also consistent with the vibrational constant of AlO(X$^2$Σ$^+$) (ω$_v$≈979 cm$^{-1}$). The vibrational states of AlO (v=0–2) are also shown at the top of FIG. 3. The ratios of peak areas in region B are AlO(v=1)/AlO(v=0)=0.69±0.02, and AlO(v=2)/AlO(v=0)=0.52±0.02, respectively. The AlO(v=0) state also makes a major contribution to the dissociation of cations. The TKER peak corresponding to AlO(v=0) obtained from the photodissociation of AlO$^+$ gives $D_0$(AlO$^+$) of 15104±40 cm$^{-1}$, which is 2194 cm$^{-1}$ higher than the value from Hildenbrand [2]. The difference may be due to part of the energy released as electron kinetic energy during the AlO ionization.

The angular distributions of Al/Al$^+$ from two photodissociation channels of AlO are shown in FIG. 4, which are described by the anisotropy parameter $\beta$ according to [30],
\[
I(\theta) = I_0 \left[ 1 + \sum_{n=1}^{\infty} \beta_{2n} P_{2n} (\cos \theta) \right] \tag{3}
\]
where $\theta$ is the angle between the polarization direction of photolysis laser and the product scattering direction, $n$ is the number of photons involved in the photolysis progress, $P_{2n}(\cos \theta)$ is 2n-th Legendre polynomial. Specifically, $n=1$ in the one-photon dissociation of AlO and $n=2$ while in the two-photon dissociation of AlO$^+$.

The angular distributions of the Al and Al$^+$ photofragments with a fit by Eq.(3) are shown in FIG. 4. The angular distributions tend to be isotropic with the increase of vibrational level of AlO. For the dissociation of neutral AlO radical, $\beta$(Al) decreases from 0.65 to 0.04 with the increase of $v$ from AlO(v=0) to AlO(v=2), while $\beta$(Al$^+$) slightly decreases from 0.19 to 0.09 with the increase of $v$ from AlO(v=0) to AlO(v=2). Therefore, the one-photon dissociation of AlO is faster than that of the two-photon dissociation of AlO$^+$, and the dissociation time of AlO strongly depends on the vibrational level of AlO.

From the above discussion, we know that some AlO radicals absorb one photon at 193 nm and direct dissociation occurs on the excited electronic state to generate Al($^3$P$_u$)+O($^3$P$_g$), meanwhile some AlO radicals can absorb two photons simultaneously and ionic dissociation occurs to produce Al$^+($0$^1$S$_g$)+O($^3$P$_g$). For AlO(v=0), the ratio of Al$^+$ to Al signal is Al$^+$/Al=0.07±0.01, indicating that the dissociation of neutral AlO is dominant. At 193 nm (51813.5 cm$^{-1}$), based on the theoretical calculation from Schamps [3] and Zhu’s group [15], the parallel transition of AlO from the ground state X$^2$Σ$^+$ to the repulsive wall of the bound state C$^2$Π(0$^+$) state would lead to the direct dissociation to Al($^3$P$_u$) and O($^3$P$_g$). After the two-photon ionization of AlO, the α$^3$II state of AlO$^+$ is energetically involved in the dissociation of AlO$^+$ and may lead to the nearly isotropic angular distribution of products [3, 31].

IV. CONCLUSION

The photodissociation dynamics of AlO at 193 nm is studied using time-sliced ion velocity imaging technique. The speed and angular distributions of products from Al$^+$ image reveal two distinct dissociation pathways: one pathway is the one-photon excitation of AlO to the repulsive wall of C$^2$Π(0$^+$) state followed by direct dissociation to the Al($^3$P$_u$) and O($^3$P$_g$), and the other pathway is the two-photon absorption to form AlO$^+$ followed by dissociation to Al$^+($0$^1$S$_g$) and O($^3$P$_g$). Among them, the dissociation dynamics to Al($^3$P$_u$) and O($^3$P$_g$) depends largely on the vibration state of the parent AlO radical. We obtain the bond dissociation

energy of AlO and AlO\(^+\) as \(D_0(\text{AlO}) = 42742 \pm 40 \text{ cm}^{-1}\) and \(D_0(\text{AlO}^+) = 15104 \pm 40 \text{ cm}^{-1}\), respectively.

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