# Effects of Size and Prestressing of Aluminum Particles on the Oxidation of Levitated *exo*-Tetrahydrodicyclopentadiene Droplets

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Cite This: J. P.	hys. Chem. A 2020, 124, 1489–1507	Read Online	
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**ABSTRACT:** Addition of high-energy-density materials such as aluminum (Al) microparticles or nanoparticles to liquid propellants potentially improves performance of the fuel. We report on the effects of untreated, prestressed, and superquenched aluminum particles with diameters of 100 nm, 250 nm, 500 nm, 1.6  $\mu$ m, and 8.8  $\mu$ m on the combustion of JP-10 droplets acoustically levitated in an oxygen-argon atmosphere. Ignition was initiated by a carbon dioxide laser, and the resulting oxidation processes were traced by Raman, Fourier-transform infrared (FTIR), and ultraviolet-visible (UV-vis) spectroscopies together with high-speed optical and IR thermal-imaging cameras. The UV-vis emission spectra reveal that the key reactive radical intermediates hydroxyl (OH), methylidyne (CH), dicarbon (C<sub>2</sub>), aluminum monoxide (AlO), and aluminum monohydride (AlH) were formed in addition to atomic aluminum (Al) and the final oxidation products of JP-10 droplets and produced higher temperatures in the combustion process of up to typically 2600 K. The effect of the Al particles on the ignition and maximum flame temperatures increased as the diameters reduced. The



different stress treatments did not produce observable changes for the ignition or combustion of the droplets, which indicates that the liquid propellant was not significantly affected by manipulating the mechanical properties of the fuel particle additive. The initiation and enhancement of the combustion were a consequence of forming highly reactive atomic oxygen (O) and aluminum monoxide (AlO) radicals in the reaction of aluminum atoms with molecular oxygen in the gas phase. These radicals initiate the degradation of JP-10 via atomic hydrogen abstraction forming the hydroxyl (OH) and aluminum hydroxide (AlOH) radicals in reactions which are mainly exothermic by up to 68 kJ mol<sup>-1</sup>. In contrast, hydrogen abstractions from JP-10 by molecular oxygen or atomic aluminum are strongly endothermic by up to 236 kJ mol<sup>-1</sup>, thus making these reactions less competitive. The generation of  $C_{10}H_{15}$  hydrocarbon radicals from the JP-10 initiates successive oxidations and chain reactions with molecular oxygen leading eventually to carbon dioxide and water. These combined experimental results provide insight into how aluminum particles facilitate the oxidation and reaction mechanisms of JP-10 droplets.

## **1. INTRODUCTION**

The hydrocarbon molecule tricyclo[ $5.2.1.0^{2,6}$ ]decane (*exo*tetrahydrodicyclopentadiene, C<sub>10</sub>H<sub>16</sub>; Scheme 1) is the major component of the hydrocarbon fuel jet propellent-10 (JP-10). JP-10 holds a high volumetric energy density of 39.6 kJ cm<sup>-3</sup> and represents the standard fuel used in air-breathing jetpropulsion missile systems.<sup>1-4</sup> The attractiveness of JP-10 as a fuel has inspired investigations that not only explore its decomposition and oxidation mechanisms but also increase its energy density and combustion efficiency.<sup>5-16</sup> Experimental work by Zhao et al.<sup>6</sup> and theoretical calculations by Morozov et al.<sup>5</sup> showed that the pyrolysis of JP-10 produces smaller hydrocarbon fragments and reactive transient species from C1 to C7 including aliphatic radicals, resonantly stabilized free radicals (RSFRs), and aromatic radicals (ARs), which initiate the oxidation of JP-10 (Scheme 2).

The improvement of the performance of air-breathing propulsion systems and JP-10 in particular requires the

development of fuels with higher energy densities than traditional hydrocarbon fuels, which are limited to a volumetric energy density of 40 kJ cm<sup>-3</sup>. The addition of high-energy-density particles such as aluminum (Al, 84 kJ cm<sup>-3</sup>) to liquid fuels represents a potential approach toward increasing the energy available from the overall reaction.<sup>17</sup> Therefore, interest in the combustion of aluminum and aluminum-doped hydrocarbon fuels has generated extensive research both experimentally<sup>18–28</sup> and theoretically.<sup>29–37</sup> The combustion of Al particles is influenced by their size, that is, the Al reactivity increases with decreasing particle diameter.<sup>18–20,34</sup> Also, the ignition temperature of Al particles decreases from 2350 K for a

Received:November 14, 2019Revised:January 16, 2020Published:February 17, 2020



Scheme 1. Molecular Structure of *exo*-Tetrahydrodicyclopentadiene  $(JP-10)^a$ 



<sup>a</sup>The carbon and hydrogen atoms are gray and white, respectively.

diameter of 100  $\mu$ m to 933 K for a diameter of 100 nm. Decreasing from micrometer- to nanometer-sized Al particles results in a reduced ignition delay, an increased flame speed, and an improved combustion efficiency.<sup>18–20,34,38</sup>

The most commonly proposed oxidation mechanism of Al particles is the diffusion-limited mechanism  $^{18-20,30,31}$  in which oxidation of the Al core is limited by diffusion of the oxidizer through the surrounding, amorphous aluminum oxide  $(Al_2O_3)$ shell. As the aluminum is oxidized, the oxide shell grows and, at a sufficiently high temperature, the aluminum oxide  $(Al_2O_3)$ undergoes a transformation from amorphous Al<sub>2</sub>O<sub>3</sub> into the crystalline, cubic form  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The aluminum core melts and therefore expands, which exerts pressure on the outer oxide layer. The expansion of the core and formation of the brittle  $\gamma$ - $Al_2O_3$  generate fractures in the oxide shell, thus increasing exposure of the Al core to the oxidizer and, hence, the oxidation rate. For nanoparticles, the energy released by reaction between the molten aluminum and the oxidizing gas ignites the particle. In contrast, the microparticles do not ignite owing to their higher thermal inertia (section 3.2). Instead, the aluminum oxide undergoes a phase transformation to form a crystalline alumina layer. The crystalline oxide layer then melts to produce a molten oxide shell or cap, which increases exposure of the aluminum core to the oxidizer. The aluminum burns from gasphase reactions, and hence particle ignition is achieved.<sup>39</sup>

The combustion of Al nanoparticles at heating rates above  $10^6$  K s<sup>-1</sup> is not described by the diffusion mechanism; an alternative oxidation model for these processes was proposed by Levitas et al., namely, the melt-dispersion mechanism.<sup>21,30,31</sup> In this model, the thickness of the oxide shell is independent of the particle diameter; therefore, as the particle size decreases,

the ratio of the radius of the Al core to the thickness of the oxide shell also decreases. If the Al:Al<sub>2</sub>O<sub>3</sub> ratio is sufficiently small, then the Al core will melt before the oxide shell fractures.<sup>21,30,31</sup> After the Al core melts, since Al has a larger thermal expansion coefficient than Al<sub>2</sub>O<sub>3</sub>, the volume of the Al increases at a greater rate than the Al<sub>2</sub>O<sub>3</sub>, which causes the internal stress of the particle to increase.<sup>21,30,31</sup> The pressure of the molten core on the outer shell (~11 GPa) triggers spallation of the oxide layer. After spallation, the pressure within the molten Al droplet remains high while the pressure at the droplet's surface approaches zero, and therefore a pressure imbalance is generated.<sup>21,30,31</sup> This pressure imbalance causes an unloading spherical wave that disperses the molten Al core into smaller fragments; these are oxidized at a higher rate, since the oxidation is no longer limited by diffusion of the oxidizer through the Al<sub>2</sub>O<sub>3</sub> shell.

The melt-dispersion mechanism suggests using the pressure between the molten core and the outer shell as a method to improve the reactivity of micrometer- to nanometer-sized particles.<sup>21,40-45</sup> To implement this approach, compressive stresses are induced within the oxide shell to strengthen the layer, which allows the molten Al core to exert an increased pressure before the shell fractures. The higher pressure increases the effect of the melt-dispersion mechanism and, hence, improves the particle's reactivity. One method to induce the required compressive stresses in the surface oxide layer is to heat the Al particles to a high temperature followed by rapid quenching.<sup>40,41,43-45</sup> Furthermore, for a sufficiently high quenching rate, the stress between the expanded Al core and the  $Al_2O_3$  shell may not have time to relax during the cooling, resulting in volumetric (or dilatational) strain energy stored in the cooled particle. The volumetric strain can be released during the ignition, thus further increasing the reactivity of the Al particles.

The quenching rate affects the stresses induced in the particles.<sup>40</sup> Quenching the Al particles at a moderately high rate such as 200 K min<sup>-1</sup> produces prestressed aluminum (PS Al) particles; quenching at the higher rate of 900 K min<sup>-1</sup> forms superquenched aluminum (SQ Al) particles. X-ray diffraction using synchrotron radiation reveals that PS Al particles and SQ Al particles have higher volumetric strain than untreated aluminum (UN Al) particles.<sup>40</sup> The volumetric strain in the SQ Al particles is lower than for the PS Al particles because delamination of the Al<sub>2</sub>O<sub>3</sub> shell from the Al core relaxes the strain for the SQ Al particles. Both treatments showed increased reactivity in impact ignition tests: the minimum impact energy required to cause ignition decreased by 83% and 89% for the PS

Scheme 2. Molecular Structures of the Free Radicals Produced in the Decomposition of JP-10 As Identified in Ref 6



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Гat	ole	1.	Summary	of	Previous	Experimental	Studies o	of Al-do	ped	JP-10	(Al/J	P-10	)
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group	Al/JP-10 sample	method	effects of adding Al	ref
Wong and Turns	40 wt % of Al slurry	Flat-flame burner	• Increased burn time	49, 50
			• Increased temperature	
			<ul> <li>Reduced ignition delay time</li> </ul>	
			• JP-10 is consumed first followed by Al combustion	
E et al.	16 wt % of 50 nm Al	Small-scale combustor	<ul> <li>Increased volumetric energy</li> </ul>	51
			<ul> <li>Increased combustion efficiency</li> </ul>	
			<ul> <li>Increased specific impulse</li> </ul>	
E et al.	1 wt % of 16 nm Al	Shock tube	• Decreased ignition delay	52
			• Increased flame intensity	
			• Increased burn time	
Luo et al.	16 wt % of 30-50 nm Al	Small-scale combustor	<ul> <li>Increased combustion efficiency</li> </ul>	56
			<ul> <li>Increased energy density</li> </ul>	
Chen et al.	10-40 wt % of 80 nm Al	Laser ignition system	• Decreased ignition time	53
			<ul> <li>Increased maximum temperature</li> </ul>	
			<ul> <li>Increased combustion efficiency</li> </ul>	
Liu et al.	30 wt % of 80 nm Al	Laser ignition system	• JP-10 burns in the early stage followed by Al burning	54
Lucas et al.	0.5 wt % of 80 nm Al	Laser ignition of ultrasonically levitated	• Required for ignition	59
		droplet	• Observed formation of OH, CH, C <sub>2</sub> , AlO radicals	

Al particles and the SQ Al particles, respectively, compared to the UN Al particles. Additionally, the SQ Al particles produced a higher combustion yield than the PS Al or UN Al samples; this was caused by delamination of the SQ Al particle's shell, which resulted in enhanced fracturing of the shell and, hence, increased oxidation of the Al core.<sup>40</sup> Recently Hill et al. studied the effects of the prestressing and superquenching for the thermal ignition of Al particles by exploiting a 600 W carbon dioxide  $(CO_2)$  laser.<sup>22</sup> The SQ Al particles were found to have the shorter burn times, whereas the PS Al particles had shorter ignition delay times. These results were explained by differences in the volumetric strain and shell delamination for the PS Al and SQ Al particles. The PS Al particles contain a higher volumetric strain, which can be released during heating to cause a decrease in the ignition delay time. In contrast, the SQ Al particles have more delaminated shells, which leads to increased fracturing of the shell and consequently to an enhanced exposure of the Al core to the oxidizer resulting in shorter burn times. These promising results motivated the present study of prestressed and superquenched Al particles in liquid propellants.

The addition of Al particles has been shown to improve the performance of hydrocarbon fuels and JP-10 in particular.<sup>46-58</sup> A summary of the experimental results for JP-10 doped with Al particles (Al/JP-10) is presented in Table 1. Wong and Turns explored the combustion of 40 wt % of aluminum slurry added to JP-10 droplets ignited in a flat-flame burner.<sup>49,50</sup> The ignition delay times were found to increase as the temperature of the flame burner decreased until the minimum ignition limit of 1300-1450 K was reached. Increasing the oxygen concentration decreased both the ignition times and burning times owing to the higher reaction rates.<sup>50</sup> Lastly, the ignition times were found to increase for larger droplet diameters. Wong and Turns also explored the burning times of pure JP-10 droplets for comparison and discovered that the aluminum-doped droplets burned four times longer than pure droplets; these experiments also established that the burning times of the pure droplets were affected by the flame burn temperature and oxygen concentration.<sup>49</sup> A three-stage ignition model of the aluminum slurry was proposed.<sup>50</sup>

E et al. synthesized 16 nm and 50 nm diameter Al NPs capped with oleic acid to reduce oxidation of the Al in the JP-10

and explored the combustion performance of the nanofluid. <sup>51,52</sup> These authors calculated that adding 30 wt % of Al NPs increases the volumetric energy density of the JP-10 by 10%.<sup>51</sup> A shock tube was used to investigate the combustion of up to 1 wt % of Al NPs in JP-10. The key discoveries were a significantly shortened ignition delay time from 521  $\mu$ s for the pure JP-10 to 213  $\mu$ s for the JP-10 doped with Al, increased burn times of the Al NP-doped fuel in the combustion process, and an increase in the intensity of the combustion flames for the Al NP doped samples.<sup>52</sup> Luo et al. utilized a small-scale combustor to study the oxidation of JP-10 containing 30-50 nm diameter Al NPs.<sup>56</sup> The aluminum doping resulted in a 3-9% higher combustion efficiency than for pure JP-10. Chen et al. recently exploited a CO<sub>2</sub> laser ignition system to study the combustion of droplets of JP-10 and JP-10 doped with 10 wt % of 80 nm Al NPs.<sup>33</sup> The addition of the Al NPs significantly decreased the ignition delays. Furthermore, combustion of the Al NP-doped droplets produced a maximum temperature of 1890 K, whereas the pure droplets reached a maximum temperature of only 1720 K. Chen et al. also discovered that increasing the Al concentration decreased the ignition delay time but reduced the degree of oxidation of the Al NPs. The combustion of JP-10 droplets doped with 10 wt % of Al was also studied in a pure oxygen atmosphere. The oxygen increased the oxidation rate of the JP-10, produced a maximum temperature of 2,116 K, and resulted in over 99% of the Al being converted to  $Al_2O_3$ .<sup>53</sup> Liu et al. utilized a CO<sub>2</sub> laser system to explore the ignition and combustion processes of JP-10 droplets containing Al NPs and the effect of varying the oxygen concentration.<sup>5</sup> Scanning electron microscope images of the aluminum oxidation products showed increased melting for higher oxygen concentrations, which suggests that higher combustion temperatures were reached and more energy was released.<sup>54</sup>

Liu et al.<sup>54</sup> proposed a model for the combustion of an Al/JP-10 droplet in air consisting of four stages: mixed combustion, liquid-evaporative combustion, microexplosion, and agglomerate combustion. In the liquid evaporation stage, a standard hydrocarbon-evaporative-diffusion flame surrounds the droplet. The combustion of JP-10 consumes oxygen on the surface of the droplet, which creates an oxygen deficiency within the droplet that prevents the immersed Al particles from reacting.

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Figure 1. Photographs of a levitated droplet of (a) pure JP-10 and JP-10 containing Al particles with diameters of (b) 100 nm, (c) 500 nm, and (d) 8.8  $\mu$ m.

In the microexplosion stage, the Al particles first form a shell on the surface of the droplet as the JP-10 burns. The Al particles that aggregate on the surface of the droplet are partially oxidized. The internal liquid fuel continues to vaporize, and the resulting pressure causes the Al surface shell to fracture thereby releasing small droplets into the flame where they burn. The final agglomerate combustion stage refers to combustion of the Al remaining on the fiber. Thus, only the Al particles released from the droplet, such as in the microexplosion or possibly carried by the evaporative-combustion of the JP-10, enter the direct flame and hence burn. Therefore, the Al combusts when not suspended in JP-10, and so the different theories of combustion for isolated Al particles, namely, the diffusionlimited mechanism and melt-dispersion mechanism, and the effects of different stress treatments should apply directly to the combustion of Al/JP-10 droplets. When there is no oxygen present, the Al particles could possibly still be oxidized by the carbon dioxide and water vapor produced in the combustion of JP-10.<sup>39</sup>

The aforementioned studies focused on how adding Al to JP-10 affects the fuel performance via parameters such as the ignition delay time, burn time, and energy released. However, the effects of the Al particles on the combustion of JP-10 at the molecular level to reveal details about the chemistry, such as the reaction intermediates and final state products, have not been elucidated. Furthermore, a systematic study of the effects of the Al particle diameter on the oxidation of Al/JP-10 has not been performed. The influence of the different stress-induced particle treatments, namely, untreated, prestressed, or superquenched, has only been studied for isolated Al particles, and so it is important to investigate the corresponding effects when the Al particles are suspended in JP-10. Such information is of critical interest to physical chemists, necessary to improve combustion models, and vital for developing the next generation of airbreathing propulsion systems. We recently reported a study of the role Al plays in the combustion of JP-10 in our work on the laser-induced oxidation of acoustically levitated droplets of JP-10 doped with untreated 100 nm diameter aluminum nanoparticles.<sup>59</sup> The combustion processes were investigated

using Raman, Fourier-transform infrared (FTIR), and ultraviolet-visible (UV-vis) spectroscopies together with highspeed optical and IR thermal-imaging cameras. In this previous study, we found that addition of 0.5 wt % of Al NPs was required to ignite the JP-10 droplets, since a droplet of pure JP-10 did not ignite under the experimental conditions. Furthermore, the spectroscopic probes revealed the formation of the hydroxyl (OH), methylidyne (CH), dicarbon (C<sub>2</sub>), and aluminum monoxide (AlO) diatomic intermediates together with water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) final state molecules in the ignition of the Al/JP-10 droplets.

Here, we extend our work on the oxidation of Al/IP-10 droplets by studying the combustion of JP-10 doped with Al particles having diameters ranging from 100 nm to 8.8  $\mu$ m to determine the effects of the Al particles size on the oxidation of JP-10. In addition to the untreated Al particles studied previously, prestressed and superquenched Al particles were also used to investigate the effects of the stress-induced treatments on the oxidation. More specifically, for the JP-10 droplets containing Al microparticles or nanoparticles with different diameters and types of treatment, we determined the percentage of oxygen  $(O_2)$ , laser power, and Al concentration required to ignite JP-10 droplets; measured the ignition and maximum temperatures; recorded the temperature temporal profiles throughout the combustion event; and collected UVvisible spectra at the instant of ignition and FTIR spectra after the oxidation is complete. The resulting, combined information is used to provide insight into how the Al particles influence the oxidation of the Al/JP-10 droplets.

## 2. EXPERIMENTAL METHODS

2.1. Acoustic Levitation Apparatus. A JP-10 droplet or an Al/JP-10 droplet were levitated in an ultrasonic levitator housed within a pressure-compatible process chamber (Figure 1).<sup>60–63</sup> The ultrasonic levitator apparatus is equipped with a piezoelectric transducer oscillating at 58 kHz and a concaveshaped reflector. A standing wave is produced by reflection of the ultrasonic sound waves between the transducer and the reflector. The sound waves exert acoustic radiation pressure on the droplet that counteracts the gravitational force, which causes the droplet to levitate slightly below one of the pressure nodes of the standing wave.<sup>64</sup> Since the acoustic radiation pressure on the droplet is only sufficient to counterbalance the gravitational force on the droplet, the acoustic pressure is too weak to effect ignition of the droplet. A microliter droplet deposition system was used to inject droplets into a pressure minimum. The deposition system consists of a syringe interfaced to the process chamber and connected to a microneedle inside the chamber using chemically inert polyetherketone (PEEK) tubing. The needle is attached to a wobble stick, which enables full translational and rotational motion. The droplets were levitated in various mixtures of oxygen (Airgas, 99.999%) and argon (Airgas, 99.9999%) at a total pressure of 864 Torr; the oxygen concentration was varied between 0% and 100% in the different experiments. The levitated droplets were oblate spheroids with a horizontal diameter of 2.7  $\pm$  0.3 mm and a vertical diameter of 1.2  $\pm$  0.3 mm, where the uncertainties represent how accurately we could control the size of the droplets for repeated droplet depositions.

A carbon dioxide laser emitting at 10.6  $\mu$ m (Synrad Firestar v40) with a repetition rate of 20 kHz was used to ignite the levitated droplets. The output power of the laser can be adjusted between 1 W and 40 W. The laser beam was focused to

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a diameter  $(1/e^2)$  of 0.2 mm on the droplet using an 8× beam expander followed by a copper parabolic mirror with a focal length of 300 mm. Raman, FTIR, and UV–vis spectroscopies were used to monitor the chemical effects of oxidizing the Al/ JP-10 droplets. The Raman spectra were collected *in situ* using a Q-switched Nd:YAG laser emitting at 532 nm. The backscattered, Raman-shifted photons were focused with a lens into a HoloSpec *f*/1.8 holographic imaging spectrograph equipped with a PI-Max 2 ICCD camera (Princeton Instruments). The spectra were collected simultaneously over the two wavenumber ranges of 300–2450 cm<sup>-1</sup> and 2400–4400 cm<sup>-1</sup>.

In the UV-vis spectrometer system, the end of a fiber-optic probe is attached to an x, y, z manipulator located inside the process chamber. The manipulator enables the probe to be precisely aligned on the droplet at a distance of approximately 6 mm. The electromagnetic radiation emitted by the igniting droplet is collected by the optical fiber, exits the chamber via a conflat fiber-optic feedthrough, and finally enters a StellarNet SILVER-Nova UV-vis spectrometer. The spectrometer operates in the 200-1100 nm spectral range with a resolution at fullwidth half-maximum (fwhm) of 2 nm. A Nicolet 6700 FTIR spectrometer (Thermo Scientific) combined with mirror optics was employed to record FTIR transmission spectra of the gases within the process chamber in the wavenumber region of 400-4000 cm<sup>-1</sup>. FTIR spectra of the unreacted, liquid samples were obtained using an attenuated total reflection (ATR) accessory located within the spectrometer. Ignition of the levitated droplets was also observed with a high-speed optical camera (Phantom Miro 3a10) recording at 1000 frames per second (fps). The video data were processed with an in-house MATLAB code to measure the burn time of each droplet. The burn time is defined as the time between the initial rise in the light intensity (or first light) and the sharp drop in the light intensity corresponding to the extinguished flame.

Ignition temperatures were determined with an IR thermalimaging camera (FLIR A6703sc) operating at 480 fps. The field of view (FOV) of the IR camera enabled the full ignition event to be observed simultaneously. The temperatures reported below are the maximum temperatures recorded within the FOV of the camera at a given time. IR thermal videos were recorded over the six temperature ranges of 283-363 K, 353-473 K, 423-623 K, 523-873 K, 773-1473 K, and 973-1773 K. An ND2 filter was attached to the camera to record in the highest three temperature ranges. The videos were converted to temporal plots of the maximum temperature using the FLIR ResearchIR Max program. The temporal profiles for each temperature range were subsequently combined to give a one plot over the full range of observed temperatures. The temperature as measured by the IR camera was calibrated by recording an IR movie in the 973-1773 K temperature range simultaneously with collecting a UV-vis spectrum of the same ignition event. A black-body fit to the background in the UVvis spectrum was used to determine the flame temperature during the first 10 ms following ignition (section 3.6). The emissivity in the ResearchIR Max program was then adjusted to give the same temperature as obtained from the black-body emission in the same time interval. The resulting value for the emissivity of the flames equal to 0.17 was used to calibrate the flame temperatures in all subsequent measurements.

**2.2. Materials.** JP-10 was purchased from BOC Sciences with a purity of  $\geq$ 98% and used without additional purification. The various JP-10 droplets were prepared by mixing JP-10 with 0.5 wt % or 2 wt % of (a) Al particles having different diameters,



Figure 2. Size distributions of the aluminum particles with mean diameters of 100 nm, 250 nm, 500 nm, 1.6 µm, and 8.8 µm.

(b) 40 nm diameter Al<sub>2</sub>O<sub>3</sub> NPs (Skyspring Nanomaterials, Inc.,  $\geq$ 98%), or (c) 3 mol % of 30–60 nm diameter yttria stabilized zirconia (YSZ; Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>; Inframat Advanced Materials; 99.9%). The untreated (UN) Al particles with nominal diameters of 80 nm, 200 nm, and 500 nm were purchased from Novacentrix; whereas the nominal 1.6  $\mu$ m and 5  $\mu$ m diameter UN Al particles were acquired from Sigma-Aldrich. The particle-size distribution was determined using a dynamic or static light-scattering particle-size analyzer (AccuSizer 780 SIS). Figure 2 shows the diameter distribution of the Al particles. The size distributions do not change significantly with prestressing or superquenching, and therefore the distributions in Figure 2 apply to all the Al particle studied below. The mean and standard deviation of the Al particle diameters for each of the manufacturer's nominal diameters are presented in Table 2

Table 2. Mean and Standard Deviation of the Al Particle Diameters for Each Nominal Diameter and the Rounded Values Quoted in the Text

nominal Al particle diameter	mean and standard deviation	quoted value
80 nm	96.1 ± 8.8 nm	100 nm
250 nm	251 ± 36 nm	250 nm
500 nm	490 ± 70 nm	500 nm
1.6 µm	$1.60 \pm 0.27 \ \mu m$	1.6 µm
5 µm	$8.8 \pm 1.2 \ \mu \mathrm{m}$	8.8 µm

together with the rounded values quoted in the text below. Details of the annealing and quenching processing are provided by Hill et al.<sup>40</sup> Briefly, powder in batch sizes of 100 mg was heated to 573 K for 10 min and then cooled in a TA Instruments Q800 dynamic mechanical analyzer (DMA). Two different quenching treatments were used to create two different volumetric strains. A quenching rate of 200 K min<sup>-1</sup> produced prestressed aluminum (PS AI) particles, and

quenching at the higher rate of 900 K min<sup>-1</sup> produced superquenched aluminum (SQ Al) particles. Generally, PS Al particles have a higher volumetric strain than the SQ Al particles.<sup>40</sup> Higher quenching rates might be expected to induce a greater volumetric strain, but delamination between the Al core and the Al<sub>2</sub>O<sub>3</sub> shell has been shown to relax the strain such that SQ Al particles have a lower strain than PS Al particles. Strain varies with particle diameter but has values of typically 9  $\times 10^{-5}$  for PS Al, 5  $\times 10^{-5}$  for SQ Al, and 1  $\times 10^{-6}$  for UN Al.<sup>40</sup>

2.3. Interaction between the Carbon Dioxide Laser Beam and the Al/JP-10 Droplets. To provide physical insight into the interaction between the carbon dioxide laser beam and the Al/JP-10 droplets, an optical model for the propagation of a carbon dioxide laser beam through a JP-10 droplet containing Al particles is developed in the Supporting Information. The key results from the model are summarized below. The CO<sub>2</sub> laser beam irradiates a spot with a diameter  $(1/e^2)$  of 0.2 mm on the surface of the droplet. The 10.6  $\mu$ m wavelength laser beam is strongly attenuated by the JP-10 such that the intensity decreases to 1/e of the value at the surface in a distance of approximately 50  $\mu$ m. The JP-10 consequently absorbs the laser beam within a thin outer layer of the droplet. Aluminum, amorphous Al<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are highly reflective to the CO<sub>2</sub> laser beam. The Al particles therefore scatter the laser beam within the thin outer layer, and most of the scattered radiation will subsequently be absorbed by the JP-10. A small fraction of the laser beam will backscatter out of the droplet, however, thereby slightly reducing the total power absorbed. Another consequence of the backscattering might be to concentrate absorption of the laser beam within a smaller volume near the surface, which could increase the probability of igniting the JP-10 droplet or vaporizing the JP-10 together with the associated ejection of the Al particles. For a given % by weight, there are fewer larger diameter Al particles in the 50  $\mu$ m outer layer relative to the smaller diameter particles from which

the  $CO_2$  laser beam can scatter, and consequently the backscattering effect is lower. The model also shows that the  $CO_2$  laser beam is mainly absorbed by the JP-10, which, in turn, heats the Al particles by thermal conduction rather than the heat transfer occurring from the Al particles to the JP-10.

#### 3. RESULTS AND DISCUSSION

**3.1. FTIR and Raman Spectroscopy before Oxidation.** Understanding the spectra of unreacted JP-10 is the first step to identify the changes caused by oxidizing the droplets. ATR-FTIR and Raman spectra of JP-10 have been reported and interpreted previously for the pure sample and when doped with 100 nm diameter untreated Al particles at a concentration of 0.5%.<sup>59</sup> Figure 3 presents the ATR-FTIR and Raman spectra



Figure 3. (a) ATR-FTIR and (b) Raman spectra of JP-10 samples containing untreated Al microparticles or nanoparticles with different diameters. The vibrational mode assignments are reported in ref 59.

of Al/JP-10 with various diameters of untreated Al particles and different Al concentrations. The addition of Al particles does not produce any new discrete peaks that are large enough to be observed in the ATR-FTIR or Raman spectra. However, the Al particles caused a broad, structureless continuum to appear upon which the JP-10 peaks were superimposed. The broad continuum, which is caused by the amorphous Al<sub>2</sub>O<sub>3</sub> shell,<sup>18–20,30,58,65,66</sup> was observed in the wavenumber region of 500–1000 cm<sup>-1</sup> in the ATR-FTIR spectrum and across the Raman spectrum. For the FTIR spectra, the backgrounds are

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mainly caused when the Al particles scatter the IR beam out of the path of the ATR accessory. The penetration depth  $d_p$  of the so-called evanescent wave within the sample is proportional to the wavelength  $\lambda$  or 1/wavenumber (Supporting Information), which explains the large rise in the background in the ATR-FTIR spectra for all the samples as the wavenumber reduces.

3.2. Minimum Ignition Conditions. There are five experimental variables in the present experiments that determine whether the droplet ignites, namely, the particle diameter, the type of stress treatment, the Al concentration, the oxygen concentration, and the laser power. The effects of the experimental variables on the oxidation processes are coupled; for example, for a given droplet type ignition might occur at an  $O_2$  concentration of 40% and a laser power of 12 W or at an  $O_2$ concentration of 30% and a laser power of 16 W. Clearly, there are too many different combinations of experimental parameters to investigate all possibilities. For example, if we varied the oxygen concentration and laser duty cycle in steps of 10% from 10% to 100%, then for five particle diameters, two Al concentrations, and three types of stress treatments there would be 3000 experiments to perform. Therefore, we can only investigate a subset of parameter space and present examples minimum ignition conditions in Table 3 and Figure 4.

Table 3. Selected Minimum Ignition Conditions of JP-10 Droplets Containing Al Particles with Different Diameters and Stress Treatments

diameter	treatment	weight (%)	O <sub>2</sub> concentration (%)	laser power (W)
100 nm	untreated	$0.5 \pm 0.1$	$40 \pm 1$	$12 \pm 1$
	prestressed	$0.5 \pm 0.1$	$40 \pm 1$	$10 \pm 1$
	superquenched	$0.5 \pm 0.1$	$40 \pm 1$	$12 \pm 1$
250 nm	untreated	$0.5 \pm 0.1$	$40 \pm 1$	$15 \pm 1$
	prestressed	$0.5 \pm 0.1$	$40 \pm 1$	$15 \pm 1$
	superquenched	$0.5 \pm 0.1$	$40 \pm 1$	$17 \pm 1$
500 nm	untreated	$2.0 \pm 0.1$	$40 \pm 1$	$25 \pm 1$
	prestressed	$2.0 \pm 0.1$	$40 \pm 1$	$27 \pm 1$
	superquenched	$2.0 \pm 0.1$	$40 \pm 1$	$27 \pm 1$
1.6 µm	untreated	$2.0 \pm 0.1$	$50 \pm 1$	$34 \pm 1$
	prestressed	$2.0 \pm 0.1$	$50 \pm 1$	$29 \pm 1$
	superquenched	$2.0 \pm 0.1$	$50 \pm 1$	$29 \pm 1$
$8.8 \ \mu m$	untreated	$2.0 \pm 0.1$	$70 \pm 1$	$25 \pm 1$
	prestressed	$2.0 \pm 0.1$	no igni	tion
	superquenched	$2.0\pm0.1$	no igni	tion

The pure JP-10 droplets did not ignite under any experimental conditions, even when levitated in 100% oxygen and for the maximum laser power of 34 W. The JP-10 droplet did not ignite in the levitator apparatus for the following reasons. First, the tightly focused laser beam caused the small, irradiated volume of JP-10 to rapidly evaporate as the temperature approached the boiling point and, hence, the evaporative cooling of the remainder of the droplet. In other words, the JP-10 evaporated before it could ignite. Second, the heating of the air around the droplet places an upper limit on the maximum temperature achievable for acoustically levitated particles.<sup>67</sup> Third, the distortion and rapid agitation of theat from the infrared laser beam. In contrast, addition of only 0.5 wt % of 100 nm diameter untreated Al NPs caused the droplet to



**Figure 4.** (a) Minimum percentage of  $O_2$  and (b) laser power required to ignite JP-10 droplets containing Al microparticles or nanoparticles with different diameters and types of stress treatment.

ignite in a 40%  $\rm O_2$  and 60% Ar gas mixture at a laser power of 12  $\pm$  1 W.

The minimum ignition conditions of the droplets are significantly affected by the Al particle diameter. First, the quantity of Al necessary to be added to the JP-10 droplets to cause ignition increased with the Al particle diameter, since the droplets doped with smaller particles (100 nm and 250 nm) only needed 0.5 wt % whereas the larger particles (500 nm, 1.6  $\mu$ m, and 8.8  $\mu$ m) required 2 wt %. Second, the laser power necessary to ignite the Al/JP-10 droplets generally increased for the larger particle diameters because the laser power required increased from  $12 \pm 1$  W to  $34 \pm 1$  W as the UN Al particle diameter increased from 100 nm to 1.6  $\mu$ m. The laser power necessary to ignite 8.8  $\mu$ m UN Al particles of 25 ± 1 W was the same as for the 500 nm diameter particles, which does not seem to follow the general trend. We note, however, that the  $O_2$ concentration was higher for the larger particles (see Table 3). Third, the minimum  $O_2$  concentration generally increased for the larger particles. Thus, the minimum O<sub>2</sub> concentrations for the 100 nm, 250 nm, and 500 nm particles was 40  $\pm$  1%; 50  $\pm$ 1% for the 1.6  $\mu$ m Al particles; and 70 ± 1% for the 8.8  $\mu$ m Al particles. Thus, decreasing the Al particle size increased the ease of ignition, which is consistent with the previously reported

relationship between the Al particle size and reactivity.<sup>18–20</sup> As a consequence of the lower surface-area-to-volume ratio, more time is required to heat a larger particle to a given temperature than a smaller particle. The decreased thermal inertia of the smaller particles might explain why a lower concentration of Al, a lower concentration of  $O_2$ , and a reduced laser power were required to ignite droplets containing smaller diameter Al particles. Another possible explanation is that there are very few larger diameter particles relative to the smaller diameter particles available for ignition (Supporting Information). The increased backscattering from the smaller Al particles could cause the laser beam to be absorbed in a smaller volume near the surface of the droplet than for the larger particles, which might also lead to the lower minimum ignition conditions (Supporting Information).

**3.3. Ignition Temperatures.** The ignition temperatures of the Al/JP-10 droplets were measured by an IR thermal-imaging camera, and the results are shown in Figure 5 and Table 4. We



**Figure 5.** Ignition temperatures (lower part of the figure below 600 K) and maximum temperatures (upper part of the figure above 1900 K) for the JP-10 droplets containing Al microparticles or nanoparticles with different diameters and types of stress treatment. The corresponding numerical values are compiled in Table 4.

## Table 4. Ignition and Maximum Temperatures of the JP-10 Droplets Containing Al Microparticles or Nanoparticles with Different Diameters and Stress Treatments

diameter	treatment	ignition temp (K)	max temp (K)
100 nm	untreated	$524 \pm 40$	$2660 \pm 260$
	prestressed	$516 \pm 38$	$2610 \pm 150$
	superquenched	$532 \pm 25$	$2510 \pm 210$
250 nm	untreated	498 ± 34	$2630 \pm 190$
	prestressed	$501 \pm 35$	$2640 \pm 180$
	superquenched	$506 \pm 26$	$2670 \pm 190$
500 nm	untreated	$511 \pm 57$	$2520 \pm 190$
	prestressed	$514 \pm 58$	$2390 \pm 210$
	superquenched	$516 \pm 55$	$2300 \pm 290$
1.6 µm	untreated	$500 \pm 55$	$2340 \pm 210$
	prestressed	$494 \pm 63$	$2330 \pm 350$
	superquenched	499 ± 62	$2430 \pm 230$
8.8 µm	untreated	$513 \pm 63$	$2300\pm270$





**Figure 6.** Temperature temporal profiles for the oxidation of various Al/JP-10 droplets levitated in a 70%  $O_2$  and 30% Ar gas mixture. The shaded areas represent the ranges of uncertainty. The start of the laser irradiation corresponds to t = 0 s.

define the ignition temperature as the temperature required to cause a droplet to ignite rather than the temperature of the combustion products after ignition. The ignition temperatures of the Al/JP-10 droplets were similar for all Al particle diameters and stress treatments and ranged from  $494 \pm 63$  K to  $524 \pm 40$  K. The boiling point of JP-10 is 458 K, and the

autoignition temperature is 509 K. After accounting for the experimental uncertainties, these temperatures suggest that the droplet ignites at temperatures comparable to the ignition temperature of JP-10. The ignition temperature of Al particles can be as low as 933 K.<sup>1,18–20</sup> Therefore, the liquid JP-10 forming the droplet ignites before the Al particles immersed within the droplet, which is consistent with previous research on the combustion of Al/JP-10 mixtures.<sup>49,50,54</sup> However, combustion is probably initiated when Al particles ejected from the droplet ignite in the path of the laser beam, which subsequently ignite the whole JP-10 droplet (section 3.7). The proposed ignition mechanism also explains why the ignition temperatures of the different JP-10 droplets are unaffected by the particle diameters and stress treatment. Droplet ignition is shown in the high-speed videos available in the Supporting Information.

Addition of Al particles was necessary for ignition under our experimental conditions (section 3.2). The Al particles could cause ignition because of the unoxidized aluminum within the particles, catalytic effects of the aluminum oxide  $(Al_2O_3)$  layer that surrounds each particle, or absorption of the laser beam in a reduced volume near the surface of the droplet produced by backscattering from the Al particles (Supporting Information). To determine the cause, experiments were performed with 2 wt % of 40 nm diameter Al<sub>2</sub>O<sub>3</sub> NPs added to JP-10 and compared with droplets containing 2 wt % of 100 nm diameter Al NPs. Droplets doped with the aluminum oxide NPs reached a maximum temperature of  $445 \pm 47$  K and rarely ignited, whereas the Al/JP-10 droplets always ignited for the same experimental conditions. Therefore, ignition of the Al/JP-10 droplets requires the unoxidized aluminum within the particles. The reason why only Al/JP-10 droplets regularly ignite is discussed in detail in section 3.7. JP-10 droplets containing yttria-stabilized zirconia (YSZ) nanoparticles were also studied, since YSZ nanoparticles are inert and so surface catalysis will not occur. The YSZ/JP-10 did not ignite for either 0.5 wt % or 2 wt %, and so these measurements indicate that inert NPs do not cause the JP-10 to ignite but a chemical process is necessary.

**3.4. Temperature Temporal Profiles and Maximum Temperatures.** The temperatures of the igniting Al/JP-10 droplets were monitored with the IR thermal-imaging camera throughout the ignition process, and the resulting temporal profiles are shown in Figure 6. Combustion of Al/JP-10 is stochastic, and so there are significant temperature variations from droplet to droplet; therefore, the profiles shown in Figure 6 were averaged over five ignitions for each Al/JP-10 droplet type with the standard deviation indicated by the shaded gray area. All droplets studied for the temperature temporal profiles contained 2 wt % of Al, were levitated in 70% O<sub>2</sub> and 30% Ar, and were irradiated with the laser power at 25  $\pm$  1 W. Combustion of the Al/JP-10 droplets was recorded with a high-speed optical camera, and representative ignitions are available in the Supporting Information videos.

The ignition event began when the levitated droplet was heated by laser irradiation, which caused the shape of the droplet to distort, gaseous JP-10 to evaporate, and aluminum particles to be released from the surface of the droplet. The temperature temporal profiles began with an increase from 300 K to approximately 500 K, followed by a larger increase to the maximum temperature. The first temperature increase corresponds to the initial heating of the droplet, and the second, larger temperature rise results from ignition and combustion. Article

The plateau in the temporal profile between the two temperature rises is probably a consequence of two main physical effects: first, evaporative cooling of the droplet as the temperature approaches, or even exceeds, the boiling point of JP-10; second, the distortion and rapid agitation of the droplet immediately prior to ignition reduce absorption of heat from the infrared laser beam. The duration of the plateau is determined by the time required to ignite the Al particles, which is a stochastic process and therefore varies in the range of approximately 10–170 ms. We note that the shorter time delays of around 10 ms are too small to be clearly observed in Figure 6. The impulsive force from the ignition and the associated heating of the surrounding gas caused the droplet to fall out of the trap<sup>67</sup> and onto the transducer below where the remaining fuel burned. A typical time between ignition and the droplet landing on the plate is  $50 \pm 5$  ms, which is similar to the free fall time of 55 ms. The temperature decreased as the droplet fell out of the trap and the fuel was consumed. After approximately 2 s, the sample had fully combusted but the surrounding environment continued to cool as the hot gases dispersed around the chamber and heat dissipated from the transducer.

The burn times of the different Al/JP-10 droplets are shown in Table 5. The burn times are for one ignition only rather than an average over five ignitions as above. Furthermore, the temperatures measured after approximately 50 ms are for the Al/JP-10 burning on the transducer plate, which will introduce additional uncertainties into the burn times and mean that the results are not directly applicable to droplets. The associated uncertainties are consequently too large to enable variations produced by the different Al particle types to be determined. We are, nevertheless, able to deduce that the burn times of the different Al/JP-10 droplets are similar, which is because the quantity of JP-10 and Al fuel available is the same for all droplets.

The maximum flame temperatures reached by the different Al/JP-10 droplets are presented in Figure 5 and Table 4. The maximum temperatures occurred 30-40 ms after ignition and therefore before the droplet made contact with the transducer plate. Clearly, the maximum temperatures increase as the Al particle sizes reduce. For example, the droplets containing the 100 nm diameter UN Al particles reached a maximum flame temperature of  $2660 \pm 260$  K, followed by the 250 nm diameter with a temperature of  $2630 \pm 190$  K, the 500 nm diameter with a temperature of 2520  $\pm$  190 K, the 1.6  $\mu$ m diameter with a temperature of 2340  $\pm$  210 K, and the 8.8  $\mu$ m diameter with a temperature of  $2300 \pm 270$  K. The observed dependence of the maximum temperature on the Al particle diameter is a consequence of differences in the surface-area-to-volume ratio. For a given concentration of Al, the total Al surface area combusting at a given time will be higher for the smaller particles, and therefore the same total energy will be released over a shorter time thereby producing a higher maximum temperature.

Table 4 reveals no clear relationship between the stress treatment type and maximum temperature. Our observation that the different treatments of the Al particles do not produce detectable changes in the ignition temperature, maximum temperature, or burn times is consistent with previous studies. Since ignition of the Al occurs for a particle ejected from the droplet (see section 3.7), the effects of the different stress treatments for isolated Al particles can be applied here. As discussed in the Introduction, the higher volumetric strain of the PS Al particles causes decreased ignition delay times. The

measurements of Hill et al.<sup>22</sup> confirm the predicted reduction in the ignition delay time from 13.79  $\mu$ s for UN Al particles to 9.37  $\mu$ s for PS Al particles. Furthermore, SQ Al particles have the shortest burn times because their delaminated shells fracture more easily and, hence, increase exposure of the Al to the oxidizer. Measurements confirm the expectation, since the burn time reduced from 1.08 ms for UN Al to 0.96 ms for SQ Al.<sup>22</sup> The reductions in the ignition delay time and burn time of only 4.42  $\mu$ s and 120  $\mu$ s, respectively, are too small to produce observable effects in the present experiments, which operate on time resolutions above 1 ms. Consequently, the ignition temperatures, maximum temperatures, and burn times are primarily affected by the particle diameter and the volume of JP-10 fuel available.

Table 5. B	urn Times	of the	Various A	Al/IP-10	Droplets
		~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~			2.000.000

diameter	treatment	burn time $(s)^a$
100 nm	untreated	$1.9 \pm 0.2$
	prestressed	$2.3 \pm 0.2$
	superquenched	$1.9 \pm 0.2$
250 nm	untreated	$2.5 \pm 0.2$
	prestressed	$2.0 \pm 0.2$
	superquenched	$2.2 \pm 0.2$
500 nm	untreated	$1.9 \pm 0.2$
	prestressed	$2.2 \pm 0.2$
	superquenched	$2.0 \pm 0.2$
1.6 µm	untreated	$2.2 \pm 0.2$
	prestressed	$2.2 \pm 0.2$
	superquenched	$2.2 \pm 0.2$
8.8 µm	untreated	$2.0 \pm 0.2$

 $^{a}\mathrm{Uncertainties}$  account for the stochastic nature of the ignition and combustion.

**3.5. Oxidation Products.** The oxidation of JP-10 forms water  $(H_2O)$  and carbon dioxide  $(CO_2)$  through the reaction

$$C_{10}H_{16}(l) + 14O_2(g) \rightarrow 10CO_2(g) + 8H_2O(g)$$
 (1)

The production of CO<sub>2</sub> and H<sub>2</sub>O in the gas phase can be monitored with the FTIR spectrometer system and thereby the quantity of these products calculated. The FTIR spectra were collected in transmission mode through the length of the process chamber a few minutes after the JP-10 had fully reacted. The initial quantity of O<sub>2</sub> can be determined using the ideal gas law. Our process chamber has a volume of 15.44 L and was filled to a total pressure of 864 Torr with 70 ± 1% O<sub>2</sub> and 30 ± 1% Ar. Therefore, initially there were 0.5026 ± 0.0093 mol of O<sub>2</sub>. Next, we determine the initial amount of JP-10 in the Al/JP-10 droplet. The droplets have a mean horizontal diameter of 2.7 ± 0.3 mm and a mean vertical diameter of  $1.2 \pm 0.3$  mm, which corresponds to a volume of  $(4.6 \pm 1.5) \times 10^{-3}$  cm<sup>3</sup>. The droplets contain 98 wt % of JP-10. Therefore, using the density of JP-10 at 0.9314 g cm<sup>-3,1</sup> the initial amount of JP-10 is determined to be  $(3.13 \pm 0.83) \times 10^{-5}$  mol. O<sub>2</sub> is the excess reactant as the initial molar ratio of O<sub>2</sub>:JP-10 is  $(1.6 \times 10^4)$ :1, which is much larger than the stoichiometric ratio of 14:1 (reaction 1).

An example of an FTIR spectrum after oxidizing an Al/JP-10 droplet is shown in Figure 7. The assignments of the bands



**Figure 7.** FTIR transmission spectrum collected after oxidizing a JP-10 droplet containing 100 nm diameter untreated Al nanoparticles previously levitated in 70%  $O_2$  and 30% Ar. The peak fits are shown together with the spectrum of JP-10 before reaction for comparison purposes (green line). The product and JP-10 rovibrational bands are labeled a–f. The wavenumbers and vibrational mode assignments of bands a–f are compiled in Table 6.

labeled a–f are compiled in Table 6. The quantities of  $CO_2$  and  $H_2O$  produced were calculated by comparing the absorbance of the  $CO_2$  asymmetric stretching mode (band d),  $CO_2$  bending mode (band f), and the OH bending mode (band e) with the known absorption cross sections of  $CO_2$  and  $H_2O$ . The reference absorption cross sections of bands d, e, and f were determined using the SPECTRA Information System<sup>68</sup> and the HITRAN molecular spectroscopic database.<sup>69</sup> The number density of the absorber, *n*, and, hence, the moles of  $CO_2$  and  $H_2O$  produced in the process chamber were calculated using the Beer–Lambert law:

$$n = \frac{A \log_{\rm e} 10}{\sigma L} \tag{2}$$

where A is the absorbance from our spectrum,  $\sigma$  is the reference absorption cross section from the database, and L is the path length of 37.6 cm. The moles of CO<sub>2</sub> and H<sub>2</sub>O produced are shown in Figure 8. Considering the large uncertainties, the

Table 6. Assignments of the Vibrational Bands in the FTIR Transmission Spectra Collected Following Oxidation of Al/JP-10

band	center wavenumber $(cm^{-1})$	molecule	number (symmetry)	vibrational mode	ref
a	3714	CO <sub>2</sub>	$ u_1(\sigma_{\mathrm{g}}^{+}) + \nu_3(\sigma_{\mathrm{u}}^{+}) $	combination band	77
Ь	3612	CO <sub>2</sub>	$ u_1(\sigma_{\rm g}^{\ +}) + \nu_3(\sigma_{\rm u}^{\ +}) $	combination band	77
с	2878, 2925, 2956	JP-10	$\nu_{57},  \nu_{62},  \nu_{68}$	CH and CH <sub>2</sub> stretch	5
d	2349	CO <sub>2</sub>	$ u_3(\sigma_{\mathrm{u}}{}^+)$	CO <sub>2</sub> asymmetric stretch	77
e	1635	$H_2O$	$ u_2(\mathrm{A}') $	OH bend	78
f	669	CO <sub>2</sub>	$ u_2(\pi_{ m u})$	CO <sub>2</sub> bend	77



**Figure 8.** Moles of (a)  $H_2O$  and (b)  $CO_2$  produced after igniting JP-10 droplets containing Al microparticles or nanoparticles with different diameters and types of stress treatment determined by comparing the FTIR spectrum in Figure 7 with reference cross sections.<sup>69</sup> The maximum numbers of moles of  $CO_2$  and  $H_2O$  that can be produced are shown by the horizontal dotted lines in (a) and (b). The observed  $CO_2:H_2O$  molar ratios for each Al/JP-10 sample are shown in (c); the stoichiometric  $CO_2:H_2O$  ratio is presented for comparison (dotted line).

experimental data in Figure 8 cannot be used to determine the effects of differences in the size and treatment of the Al particles on the moles of  $CO_2$  and  $H_2O$  produced. The moles of  $CO_2$  and  $H_2O$  formed for complete combustion of the droplet are represented by the horizontal dotted lines in Figure 8a and

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Figure 8b (reaction 1). The quantity of  $CO_2$  produced was significantly less than the yield for complete reaction, which suggests that the JP-10 only combusted partially. The competition between the formation of  $CO_2$  (reaction 1) and soot leads to the incomplete combustion of hydrocarbon fuels.<sup>70,71</sup> Previous pyrolysis and combustion studies of JP-10 have shown that the precursors of soot such as RSFRs and ARs are formed.<sup>5–16</sup> Therefore, the black soot-like residue covering the inside of the process chamber following combustion of the Al/JP-10 droplets accounts for the incomplete combustion of JP-10 via reaction 1. In Figure 8c, the observed CO<sub>2</sub>:H<sub>2</sub>O molar ratios are compared with the expected stoichiometric ratio of 1.25. The actual  $CO_2$ :H<sub>2</sub>O molar ratios are significantly higher than the stoichiometric value probably because H<sub>2</sub>O condensed on surfaces within the process chamber where it could not be detected by the FTIR spectrometer.

3.6. Ultraviolet-Visible Spectroscopy. UV-vis emission spectra were recorded in the 250-1100 nm wavelength range to identify the reactive intermediates, the individual atoms, and the final state molecules produced by oxidation of the Alcontaining JP-10 droplets. The ignition produced a black-body spectrum and emission lines for a period shorter than 10 ms, which corresponds to the highest temperatures reached immediately after ignition (see section 3.4). The UV-vis spectra were recorded sequentially with a period of 1.7 ms over the duration of the ignition event and then summed to give the final spectra presented below. The visible portion of the blackbody spectrum was observed by eye as a bright flash of light following each ignition. The combusting droplet remained levitated in a region close to the end of the fiber-optic probe throughout the data collection period. A UV-vis emission spectrum is shown in Figure 9 for the example of the 500 nm



**Figure 9.** UV–vis emission spectrum produced by ignition of a JP-10 droplet containing 500 nm diameter untreated aluminum particles. The fit was obtained by simultaneously optimizing a black-body background (blue line) and 32 Gaussian peaks (green lines) over the 265–1040 nm wavelength range.

diameter untreated Al particles. The fit in Figure 9 was obtained by simultaneously optimizing a black-body background (blue line) and 32 Gaussian peaks (green lines). The fitted Gaussian peaks enabled the wavelengths and amplitudes of the emission peaks to be determined, while the optimized black-body function was used to determine the ignition temperature and yielded  $2670 \pm 50$  K. To show the emission structure with improved clarity, in Figure 10 the same data are presented but with the black-body spectrum subtracted. The band centers for the molecules and emission line wavelengths for the atoms of



**Figure 10.** The same spectrum as shown Figure 9 except the blackbody background has been subtracted to show the emission peaks or bands with improved clarity. The assignments of bands a-t are presented in Table 7.

most prominent features are presented in Table 7 together with the spectral assignments. Emissions from the OH, C<sub>2</sub>, and CH radicals are known to dominate the UV–vis spectra of hydrocarbon flames,<sup>72</sup> which is also the case for the present measurements. Thus, the peak at 310 nm and the smaller structure at around 290 nm are assigned to the (2, 1) and (1, 0) bands of the OH (A  ${}^{2}\Sigma^{+}-X {}^{2}\Pi$ ) transition, respectively, where Article

 $(\nu', \nu'')$  denotes the vibrational quantum number of the lower state,  $\nu'$ , and upper state,  $\nu''$ . Peak f at 432 nm is produced by the CH (A <sup>2</sup> $\Delta$ -X <sup>2</sup> $\Pi$ ) transition. The  $\Delta \nu = \nu' - \nu'' = 1$  and 0 bands of the C<sub>2</sub> (A  ${}^{3}\Pi_{e}$ -X  ${}^{3}\Pi_{u}$ ) transition contribute to the prominent peaks i and k at 470 and 513 nm, respectively; the  $\Delta \nu = 2$  transition forms a small shoulder on the side of peak f; and the (1, 3) band adds to the broad structure around 610 nm. Aluminum produces significant structure across the 390-520 nm wavelength region. The  $\Delta \nu = 2, 1, 0, \text{ and } -1$  transitions of aluminum monoxide (AlO) (A  ${}^{2}\Sigma^{+}$ -X  ${}^{2}\Sigma^{+}$ ) contribute to the four bands centered at 455 nm, 470 nm, 486 nm, and 513 nm, respectively. The observation of several AlO bands is consistent with previous studies of aluminum monoxide flame emission spectra.<sup>73</sup> The Al( $3s^23p {}^{2}P^{\circ}_{1/2,3/2} - 3s^24s {}^{2}S_{1/2}$ ) atomic emission doublet observed at 394 nm provides evidence for the formation of individual Al atoms. The largest features in the aluminum monohydride (AlH) emission spectrum occur at 426 nm and 436 nm, which are assigned to the (0, 0) and (1, 1)bands of the A  ${}^{1}\Pi \rightarrow X {}^{1}\Sigma^{+}$  transition, respectively.<sup>74</sup> The intensity of the (1, 1) band is approximately 30% that of the (0, 1)0) band. Therefore, the small shoulder at 426 nm provides tentative evidence for the formation of AlH in the oxidation processes. Sodium, an impurity found in all Al particles, produced the  ${}^{2}S_{1/2} - {}^{2}P_{3/2}$  and  ${}^{2}S_{1/2} - {}^{2}P_{1/2}$  unresolved emission doublet at 589 nm. The wavelength region from approximately 600 to 900 nm is dominated by emissions from water molecules

Table 7. Vibrational Mode Assignments for the Peaks or Bands in the UV–Vis Emission Spectrum Produced by Ignition of JP-10 Containing Al Particles

peak or band	peak wavelength or band center <sup>a</sup> (nm)	molecule	ref wavelength (nm) <sup>b</sup>	transition	branch; vibrational quantum numbers $(\nu', \nu'')$ or $(\nu_1', \nu_2', \nu_3') - (\nu_1'', \nu_2'', \nu_3'')$
a	283	OH	281.1–282.9 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Pi$	$R_1, R_2, Q_1, Q_2; (1, 0)$
b	291	OH	287.5–289.3 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Pi$	$R_1, R_2, Q_1, Q_2; (2, 1)$
c	310	OH	309.0 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Pi$	Q <sub>2</sub> ; (0, 0)
d	394	Al	394.4006 <sup>c</sup>	$3s^23p \ ^2P^{\circ}_{1/2} - 3s^24s \ ^2S_{1/2}$	
		Al	396.152 <sup>c</sup>	$3s^23p\ ^2P^{\circ}_{\ 3/2}-3s^24s\ ^2S_{1/2}$	
e	426	AlH	426.1 <sup>d</sup>	A ${}^{1}\Pi \rightarrow X {}^{1}\Sigma^{+}$	(0, 0)
f	432	CH	431.4 <sup>b</sup>	A $^{2}\Delta$ -X $^{2}\Pi$	Q <sub>i</sub> (0,0)
g	439	$C_2$	438.2 <sup>b</sup>	A ${}^{3}\Pi_{g}$ -X ${}^{3}\Pi_{u}$	(2, 0)
h	455	AlO	453.8 <sup>b</sup>	A ${}^{2}\Sigma^{+}$ -X ${}^{2}\Sigma^{+}$	(5, 3)
i	470	AlO	467.2 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(2,1)
		AlO	469.5 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(3, 2)
		$C_2$	469.8 <sup>b</sup>	A ${}^{3}\Pi_{g}$ – X ${}^{3}\Pi_{u}$	(3, 2)
j	486	AlO	484.2 <sup>b</sup>	A ${}^{2}\Sigma^{+}$ -X ${}^{2}\Sigma^{+}$	(0, 0)
		AlO	486.6 <sup>b</sup>	A ${}^{2}\Sigma^{+}$ -X ${}^{2}\Sigma^{+}$	(1, 1)
k	513	AlO	507.9 <sup>b</sup>	A ${}^{2}\Sigma^{+}$ -X ${}^{2}\Sigma^{+}$	(0, 1)
		AlO	510.2 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(1, 2)
		AlO	512.3 <sup>b</sup>	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(2, 3)
		$C_2$	512.9 <sup>b</sup>	A ${}^{3}\Pi_{g}$ -X ${}^{3}\Pi_{u}$	(1, 1)
		$C_2$	516.5 <sup>b</sup>	A ${}^{3}\Pi_{g}$ -X ${}^{3}\Pi_{u}$	(0, 0)
1	542				
m	589	Na	589.59 <sup>c</sup>	${}^{2}S_{1/2} - {}^{2}P_{3/2}$	
			589.00 <sup>c</sup>	${}^{2}S_{1/2} - {}^{2}P_{1/2}$	
n	612 (v broad)	$C_2$	612.2 <sup>b</sup>	$A^{3}\Pi_{g} - X^{3}\Pi_{u}$	(1, 3)
0	650 (v broad)	$H_2O$	646–663 <sup>e</sup>	rovib mode	(3, 0, 1) - (0, 0, 0)
р	679				
q	705	$H_2O$	690-710 <sup>e</sup>	rovib mode	(1, 0, 3) - (0, 0, 0)
r	754 (v broad)	$H_2O$	712-737 <sup>e</sup>	rovib mode	(3, 0, 1) - (0, 0, 0)
s	840 (v broad)	$H_2O$	811-839 <sup>e</sup>	rovib. mode	(2, 1, 1) - (0, 0, 0)
t	939, 992	$H_2O$	928–966 <sup>e</sup>	rovib mode	(2, 0, 1) - (0, 0, 0)

<sup>a</sup>Measurements are accurate to within 1 nm. <sup>b</sup>Reference 72. <sup>c</sup>Reference 76. <sup>d</sup>Reference 74. <sup>e</sup>Reference 69.

in highly excited vibrational states. Similar structure is observed in the emission spectrum of hydrogen flames.<sup>75</sup> Furthermore, modeling the absorption spectrum of water vapor at temperatures of around 2500 K produces similar overall, broad features in the same wavelength range;<sup>69</sup> the bands are observed to broaden and extend to longer wavelengths as the temperature rises. In Table 7, the combination bands of water are designated by  $(\nu_1, \nu_2, \nu_3)$ , where  $\nu_1, \nu_2$ , and  $\nu_3$  represent the O-H symmetric stretch, the H-O-H bend, and the O-H asymmetric stretch of the water molecule at 2734 nm (3657 cm<sup>-1</sup>), 6269 nm (1595 cm<sup>-1</sup>), and 2662 nm (3756 cm<sup>-1</sup>), respectively. For example, the broad structure centered at 840 nm  $(11\,900\,\text{cm}^{-1})$  is caused by the transition from the (2, 1, 1)combination band to the vibrational ground state (0, 0, 0). The broad absorption region from about 900 to 1000 nm (or 11 110 to 10 000 cm<sup>-1</sup>) closely resembles the (2, 0, 1) - (0, 0, 0)combination band of water vapor, but the structure in this region is complicated by absorption from the optical fiber which makes simple interpretation here impracticable. The effects of the size and prestressing of aluminum particles on the UV-vis emission spectra are discussed in Supporting Information.

Finally, we consider how the emission lines are produced. To form the OH peak at 310 nm, for example, with the corresponding excitation energy, *E*, of  $6.41 \times 10^{-19}$  J would require a temperature,  $E/k_{\rm B}$ , of  $4.6 \times 10^4$  K to be created thermally, which is greatly in excess of the highest temperatures reached at around 2900 K. Emission lines in the UV–vis spectra are thus caused by chemiluminescence, in which radicals are produced in electronically excited states via chemical reactions. The possible chemical reactions producing the excited species<sup>72</sup> are listed below together with the enthalpies of reaction,  $\Delta_r H_{\rm gas}$ , the electronic excitation energy per mole,  $\Delta_{\rm electronic}$  and the Gibbs free energy of the reaction,  $\Delta_r G_{\rm gas}$ , at a typical ignition temperature of 2500 K.<sup>76</sup>

OH:

$$CH + O_2 \rightarrow CO + OH^*$$
,  $\Delta_r H_{gas}(298 \text{ K}) = -666 \text{ kJ mol}^{-1}$   
 $\Delta_r G_{gas}(2500 \text{ K}) = -632 \text{ kJ mol}^{-1}$   
 $\Delta_{electronic}(OH) = 386 \text{ kJ mol}^{-1}$ 
(3)

where \* denotes an electronically excited state. C<sub>2</sub>:

$$C + CH \rightarrow C_2^* + H, \ \Delta_r H_{gas}(298 \text{ K}) = -255 \text{ kJ mol}^{-1}$$
  
 $\Delta_r G_{gas}(2500 \text{ K}) = -212 \text{ kJ mol}^{-1}$   
 $\Delta_{electronic}(C_2) = 233 \text{ kJ mol}^{-1}$  (4)

where the atomic carbon is most likely produced by

 $CH + H \rightarrow C + H_2$ 

CH:

$$C_2 + OH \rightarrow CO + CH^*$$
,  $\Delta_r H_{gas}(298 \text{ K}) = -393 \text{ kJ mol}^{-1}$   
 $\Delta_r G_{gas}(2500 \text{ K}) = -369 \text{ kJ mol}^{-1}$   
 $\Delta_{electronic}(CH) = 278 \text{ kJ mol}^{-1}$ 
(5)

$$\begin{aligned} \mathrm{OH} + \mathrm{H} &\to \mathrm{H_2O^*}, \ \ \Delta_{\mathrm{r}} H_{\mathrm{gas}}(298 \ \mathrm{K}) = -499 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \\ \Delta_{\mathrm{r}} G_{\mathrm{gas}}(2500 \ \mathrm{K}) = -167 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \\ \Delta_{\mathrm{electronic}}(\mathrm{H_2O}) = 160 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \end{aligned} \tag{6}$$

 $AlO_{gas}$ :

$$\begin{aligned} \text{Al}_{\text{gas}} + \text{O} &\to \text{AlO}^*, \quad \Delta_r H_{\text{gas}}(298 \text{ K}) = -512 \text{ kJ mol}^{-1} \\ \Delta_r G_{\text{gas}}(298 \text{ K}) = -480 \text{ kJ mol}^{-1} \\ \Delta_{\text{electronic}}(\text{AlO}) = 246 \text{ kJ mol}^{-1} \end{aligned}$$
(7)

AlH<sub>gas</sub>:

$$\begin{aligned} \mathrm{Al}_{\mathrm{gas}} + \mathrm{H} &\to \mathrm{AlH}_{\mathrm{gas}}^{*}, \quad \Delta_{\mathrm{r}} H_{\mathrm{gas}}(298\,\mathrm{K}) = -289\,\mathrm{kJ\,mol^{-1}}\\ \Delta_{\mathrm{r}} G_{\mathrm{gas}}(2800\,\mathrm{K}) = 14\,\mathrm{kJ\,mol^{-1}}\\ \Delta_{\mathrm{electronic}}(\mathrm{AlH}) = 281\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{8}$$

The proposed reactions thus release sufficient energy to excite the electronic states. For reaction 7, the Gibbs free energy of reaction,  $\Delta_r G_{gas}$ , was not calculated at 2500 K because the entropy  $S^{\circ}_{gas}$  and enthalpy of formation  $\Delta_f H^{\circ}_{gas}$  are unavailable for atomic oxygen above 298 K. For reaction 8,  $\Delta_r G_{gas}$  is given for 2800 K because  $S^{\circ}_{gas}$  and  $\Delta_f H^{\circ}_{gas}$  for Al are available for 298 K and temperatures above 2791 K only.<sup>76</sup>

3.7. Ignition and Reaction Mechanisms. We discuss, first, the experimental mechanism by which the JP-10 droplets are ignited in the levitator; second, we consider the steps in the chemical reactions leading to the ignition. The laser beam with powers of up to 40 W is tightly focused onto a spot on the droplet with a diameter of only 0.2 mm. A very small volume of the droplet is therefore rapidly heated, which results in a plume of Al particles being ejected at high speed from the surface in addition to evaporation of the JP-10 (videos in Supporting Information). An ejected Al particle crossing the path of the infrared laser beam in the  $O_2$ -Ar atmosphere ignites (videos in Supporting Information), which, in turn, causes the nearby Al particles and JP-10 vapor to ignite. Finally, the cloud of burning Al particles and JP-10 vapor close to the droplet ignites the whole JP-10 droplet. The above mechanism explains why, in contrast to pure JP-10, droplets of JP-10 containing Al particles ignite.

We next discuss the underlying reaction mechanisms by which the aluminum particles facilitate oxidation of the JP-10. First, the heating of an Al particle by the laser with the intensities of up to  $10^5$  W cm<sup>-2</sup> causes the oxide shell to fracture or melt and the aluminum core to melt and evaporate. Highly reactive atomic oxygen (O) and aluminum monoxide (AlO) radicals are formed by reaction between the gaseous aluminum so produced and molecular oxygen:

$$Al + O_2 \rightarrow AlO + O$$
  $\Delta H_R(0 \text{ K}) = -14 \text{ kJ mol}^{-1}$ 
(9)

which has no entrance barrier.<sup>48</sup> Both atomic oxygen and aluminum monoxide can abstract atomic hydrogen from either of the six chemically nonequivalent C–H bonds of JP-10 (Schemes 3 and 4) mainly in exothermic reactions forming the hydroxyl (OH) and aluminum hydroxide (AlOH) radicals, respectively (reactions 10 and 11). Further steps in this chain may produce aluminum dioxide (AlO<sub>2</sub>).<sup>48</sup>

$$O + C_{10}H_{16} \rightarrow C_{10}H_{15} + OH$$
$$\Delta H_r(0 \text{ K}) = -29 \text{ to } +11 \text{ kJ mol}^{-1}$$
(10)

 $H_2O:$ 

Scheme 3. Abstraction of Atomic Hydrogen (H) from Either of the Six Chemically Nonequivalent C–H Bonds of JP-10 by Atomic Oxygen (O) To Form Hydroxyl (OH) Radicals<sup>*a*</sup>



"The computed reaction enthalpies,  $\Delta H_{\rm r}(0~{\rm K})$ , are in units of kJ mol<sup>-1</sup>.

Scheme 4. Abstraction of Atomic Hydrogen (H) from Either of the Six Chemically Nonequivalent C–H Bonds of JP-10 by Aluminum Monoxide Radicals (AIO) To Form Aluminum Hydroxide (AIOH)<sup>*a*</sup>



 $^{a}\mathrm{The}$  computed reaction enthalpies,  $\Delta H_{\mathrm{r}}(0~\mathrm{K}),$  are in units of kJ mol^{-1}.

AlO + 
$$C_{10}H_{16} \rightarrow C_{10}H_{15}$$
 + AlOH  
 $\Delta H_r(0 \text{ K}) = -64 \text{ to } -24 \text{ kJ mol}^{-1}$  (11)

The heat of formation,  $\Delta H_{\rm f}(0 \text{ K})$ , for aluminum hydride oxide, H–Al = O, at –2 kJ mol<sup>-1</sup> is 176 kJ mol<sup>-1</sup> higher than for aluminum hydroxide, Al–O–H, and therefore HAlO is less

likely to contribute to the reactions. In contrast to reactions 10 and 11, hydrogen abstraction from JP-10 by molecular oxygen via reaction 12 is strongly endoergic with enthalpies of reaction,  $\Delta H_{\rm r}(0~{\rm K})$ , ranging from +196 to +236 kJ mol<sup>-1</sup> (Scheme 5).

Scheme 5. Abstraction of Atomic Hydrogen (H) from Either of the Six Chemically Nonequivalent C–H Bonds of JP-10 by Molecular Oxygen  $(O_2)$  To Form Hydrogen Peroxide Radicals  $(HO_2)^a$ 



<sup>*a*</sup>The computed reaction enthalpies,  $\Delta H_r(0 \text{ K})$ , are in units of kJ mol<sup>-1</sup>.

Likewise, hydrogen abstraction from JP-10 by atomic aluminum is endoergic (reaction 13 ; Scheme 6).

$$O_{2} + C_{10}H_{16} \rightarrow C_{10}H_{15} + O_{2}H$$
  

$$\Delta H_{r}(0 \text{ K}) = 196 \text{ to } 236 \text{ kJ mol}^{-1}$$
(12)

$$AI + C_{10}H_{16} \rightarrow C_{10}H_{15} + AIH$$
$$\Delta H_{r}(0 \text{ K}) = 102 \text{ to } 142 \text{ kJ mol}^{-1}$$
(13)

Therefore, these considerations suggest that the oxidation products of aluminum, namely, atomic oxygen and aluminum monoxide (reaction 9), abstract atomic hydrogen from JP-10 more efficiently via reactions 10 and 11 than molecular oxygen and atomic aluminum by reactions 12 and 13, respectively. These findings are consistent with our experimental result that Al particles are required to ignite the JP-10 droplet. The conclusion that oxidation of Al-containing JP-10 is dominated by a chain mechanism involving Al rather than the direct oxidation of the JP-10 by molecular oxygen is supported by studies of a composite fuel consisting of *n*-decane or methane and aluminum nanoparticles. Smirnov et al.<sup>48</sup> calculated that the rate for reaction 9 is a factor of 10<sup>9</sup> larger than for the direct oxidation of *n*-decane by molecular oxygen (cf. reaction 12).

## 4. CONCLUSION

We acoustically levitated aluminum-doped JP-10 droplets in an oxygen-argon atmosphere and ignited the droplets using a carbon dioxide laser. The resulting oxidation processes were

Scheme 6. Abstraction of Atomic Hydrogen (H) from Either of the Six Chemically Nonequivalent C-H Bonds of JP-10 by Atomic Aluminum (Al) To Form Aluminum Monohydride Radicals (AlH)<sup>*a*</sup>



<sup>*a*</sup>The computed reaction enthalpies,  $\Delta H_r(0 \text{ K})$ , are in units of kJ mol<sup>-1</sup>.

studied by Raman, FTIR, and UV–vis spectroscopies together with high-speed optical and IR thermal imaging cameras. The Al particles had diameters of 100 nm, 250 nm, 500 nm, 1.6  $\mu$ m, or 8.8  $\mu$ m and were prepared with three different treatments: untreated, prestressed, and superquenched. Our objective was to investigate how the different particle diameters and stress treatments affect key experimental parameters such as the minimum ignition conditions, ignition and maximum temperatures, temperature temporal profiles, and the product yields.

The minimum ignition conditions of the droplets are significantly affected by the Al particle diameter. Thus, a lower concentration of Al, a lower concentration of  $O_2$ , and a reduced laser power were required to ignite droplets containing smaller diameter Al particles. The smaller particles probably ignited more easily because their lower surface-area-to-volume ratio resulted in a decreased thermal inertia. JP-10 droplets doped with 2 wt % of 40 nm diameter Al<sub>2</sub>O<sub>3</sub> NPs rarely ignited, which shows that the Al/JP-10 droplets ignited owing to the unoxidized aluminum within the Al particle's core.

The ignition temperatures of the Al/JP-10 droplets were similar for all Al particle diameters and stress treatments and ranged from 494  $\pm$  63 K to 524  $\pm$  40 K. These ignition temperatures are comparable to the autoignition temperature of JP-10 at 509 K but are well below the lowest ignition temperature of 933 K for Al particles. Therefore, the liquid JP-10 forming the droplet ignited before the Al particles immersed within the droplet. However, ignition was most likely triggered when a very small volume of Al particles ejected from the droplet were ignited by the tightly focused laser beam. The 100 nm and 8.8  $\mu$ m diameter particles produced maximum temperatures of 2660  $\pm$  260 K and 2300  $\pm$  270 K, respectively. The maximum temperatures are higher for the smaller particles owing to their increased surface-area-to-volume ratio. In the temperature temporal profiles, the first temperature increase

corresponds to the initial heating of the droplet, whereas the second, larger temperature rise results from ignition and combustion. The plateau in the temporal profile between the two temperature rises was probably partially caused by evaporative cooling of the droplet as the temperature approached the boiling point of JP-10. The burn times of the different Al/JP-10 droplets are similar, which is because the quantity of JP-10 and Al fuel available is the same for all droplet types. Our observation that the different stress treatments of the Al particles did not produce detectable changes in the minimum ignition conditions, ignition and maximum temperatures, or burn times is consistent with previous measurements.<sup>22</sup> The reductions in the ignition delay time and burn time of only 4  $\mu$ s and 120  $\mu$ s, respectively, caused by prestressing are too small to produce observable effects in the present experiments which operate on time resolutions above 1 ms.

The ignition mechanisms differ for an Al-containing droplet in the levitator apparatus and for the combustion conditions within an engine. In the levitator, ignition was initiated when a very small volume of ejected Al particles were ignited by a tightly focused laser beam, whereas in an engine the JP-10 ignites before the Al because of the elevated ambient temperatures. However, after the burning Al particles cause the levitated JP-10 droplet to ignite as a whole, the combustion processes should proceed in essentially the same way as for a droplet combusting within an engine. Therefore, our conclusions regarding the effects of the Al particles on the combustion of JP-10 are expected to apply to droplets within an engine, with the possible exception of the minimum ignition conditions discussed in section 3.2.

UV-vis emission spectra were collected to identify the reactive intermediates, the individual atoms, and the final state molecules produced by oxidation of the Al-containing JP-10 droplets. The 280–600 nm wavelength range is dominated by emissions from the diatomic radical intermediates hydroxyl (OH), methylidyne (CH), dicarbon ( $C_2$ ), aluminum monoxide (AlO), and aluminum monohydride (AlH) in addition to atomic aluminum (Al). Prominent features in the region from 600 to 900 nm were assigned to emissions from water molecules in highly excited vibrational states.

Thus, the micrometer- to nanometer-sized Al particles facilitated ignition of the JP-10 droplets and produced higher temperatures. The enhanced combustion was most likely a consequence of forming atomic oxygen (O) and aluminum monoxide (AlO) radicals by the rapid reaction between gaseous aluminum and molecular oxygen. The O and AlO radicals subsequently abstract atomic hydrogen from JP-10 to form organic radicals such as  $C_{10}H_{15}$ , which can be oxidized by molecular oxygen via barrierless radical–radical reactions. Overall, our investigations show that adding aluminum particles to JP-10 is a promising approach to improve the performance of propulsion systems exploiting JP-10.

#### ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.9b10697.

(1) Optical model for the propagation of a carbon dioxide laser beam through a JP-10 droplet containing Al particles, (2) effects of size and prestressing of aluminum particles on the UV-visible emission spectra produced

by igniting levitated JP-10 droplets, and (3) descriptions of high-speed optical videos of droplet ignition (PDF) High-speed video of an igniting JP-10 droplet doped with 100 nm diameter untreated Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 100 nm diameter prestressed Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 100 nm diameter superquenched Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 250 nm diameter untreated Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 250 nm diameter prestressed Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 250 nm diameter superquenched Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 500 nm diameter untreated Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 500 nm diameter prestressed Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 500 nm diameter superquenched Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 1.6  $\mu$ m diameter untreated Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 1.6  $\mu$ m diameter prestressed Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with 1.6  $\mu$ m diameter superquenched Al particles (MP4) High-speed video of an igniting JP-10 droplet doped with

8.8  $\mu$ m diameter untreated Al particles (MP4)

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## **Author Contributions**

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under Contract N000141912083. Al particle production was supported by the Office of Naval Research under Grant N00014-19-1-2082 (Texas Tech University).

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