

Effects of Nitrogen Dioxide on the Oxidation of Levitated *exo*-Tetrahydrodicyclopentadiene (JP-10) Droplets Doped with Aluminum Nanoparticles

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hydrocarbon fuels, but the effect of NO₂ on the ignition of fuels with energy densities enhanced by aluminum (Al) nanoparticles has not been studied. We therefore investigated the effects of NO₂ on the ignition of JP-10 droplets containing Al nanoparticles initially acoustically levitated in an oxygen—argon mixture. A carbon dioxide laser ignited the droplet and the resulting combustion processes were traced in real time using Raman, ultraviolet—visible (UV—vis), and Fourier-transform infrared (FTIR) spectroscopies simultaneously with a high-speed optical or thermal imaging camera. Temperature temporal profiles of the ignition processes revealed that a 5% concentration of NO₂ did not cause measurable differences in the ignition delay time or the initial rate of temperature rise, but the maximum flame temperature was reduced from 2930 \pm 120 K to 2520 \pm 160 K. The relative amplitudes of the UV—vis emission bands were used to deduce how NO₂ affected the composition of the radical pool



during the oxidation process; for example, the radicals NO, NH, and CN were detected and the OH (A ${}^{2}\Sigma^{+}-X {}^{2}\Pi$) band at 310 nm was less prominent with NO₂. Localized heating from a tightly focused infrared laser beam provided sufficient energy to activate chemical reactions between the JP-10 and NO₂ without igniting the droplet. Raman spectra of the residue produced give information about the initial oxidation mechanisms and suggest that organic nitro compounds formed. Thus, in contrast to previous studies of hydrocarbon combustion without Al nanoparticles, NO₂ was found not to enhance the ignition of an Al-doped JP-10 droplet ignited by a CO₂ laser.

1. INTRODUCTION

Two mechanisms can introduce significant concentrations of nitrogen dioxide (NO_2) into the fuel-air mixture within an internal combustion engine before ignition. First, in exhaust gas recirculation (EGR), a portion of the exhaust from the engine is recirculated into the combustor, which dilutes the fuel-air mixture with nitrogen dioxide in addition to carbon dioxide (CO₂), carbon monoxide (CO), water (H₂O), and unburned hydrocarbons.¹ Second, alkyl nitrates and particularly 2-ethylhexylnitrate (EHN, $CH_3(CH_2)_3CH(C_2H_5)$ -CH₂ONO₂) are frequently added to improve the ignition quality of hydrocarbon fuels in diesel engines, and these organic nitrates dissociate to form an alkoxy radical (RO) and nitrogen dioxide.² Nitrogen dioxide promotes the oxidation of a hydrocarbon fuel by converting less reactive radicals such as methyl (CH_3) , hydroperoxyl (HO_2) , and methyldioxy (CH₃O₂) into highly reactive radicals including hydroxyl (OH) and methoxy (CH_3O) , which initiate the oxidative degradation of the hydrocarbon fuel and consequently accelerate the ignition (section 3). Experimental measurements and theoretical calculations confirm that nitrogen dioxide and nitric oxide (NO) significantly reduce the ignition delay time of a fuel, 3^{-13} where the ignition delay time is defined as the

period between the start of injecting fuel into the combustion chamber and the start of combustion.¹ A shorter ignition delay time improves the ignition quality of a fuel by increasing, for example, the cetane number, the fuel conversion efficiency, and the power output.¹ Chemical kinetic models describing reactions between hydrocarbon fuels and nitrogen dioxide involving several hundred species and a few thousand reactions have been developed.¹⁴

The volumetric energy density of 39.6 kJ cm⁻³, high thermal stability, and low freezing point make the hydrocarbon fuel tricyclo[$5.2.1.0^{2.6}$]decane (exo-tetrahydrodicyclopentadiene; $C_{10}H_{16}$; Scheme 1) or Jet Propulsion 10 (JP-10) ideal for use in air-breathing jet-propulsion missile systems.^{15–18} JP-10 has therefore been widely studied by experimental and theoretical methods to understand its thermal decomposition and oxidation processes in air.¹⁹ However, the maximum

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



^aThe carbon and hydrogen atoms are represented by the grey and white spheres, respectively.

volumetric energy density available from conventional hydrocarbon fuels including JP-10 cannot exceed 40 kJ cm⁻³. To improve the performance of jet-propulsion systems, the energy density of JP-10 therefore needs to be enhanced by, for example, incorporating high energy-density solids such as the combustible metal aluminum (Al) with an energy density of 84 kJ cm⁻³.²⁰ The incorporation of Al microparticles or nanoparticles in JP-10 increases the combustion efficiencies, the maximum flame temperatures, and the burn times in addition to lowering the ignition delay times.^{21,22}

We previously studied the effects on the combustion of incorporating different types of Al particles in JP-10 droplets acoustically levitated in an oxygen—argon mixture.^{21,23,24} The aluminum-containing JP-10 droplets were ignited by a carbon

dioxide laser. The resulting oxidation processes were traced using Fourier-transform infrared (FTIR), ultraviolet-visible (UV-vis), and Raman spectroscopies together with high-speed optical and infrared thermal imaging cameras. These studies revealed several new effects of Al microparticles or nanoparticles on the combustion of JP-10. First, the Al particles initiated the ignition of the JP-10 droplet and produced a rapid rate of temperature rise immediately after ignition. Second, the different types of stress treatment, namely untreated, prestressed, and superquenched, did not cause observable differences.²¹ Third, the effects of the Al particles increased when the diameter was reduced from the micrometer scale to the nanometer scale. Finally, Al nanoparticles manufactured by acetonitrile-assisted ball milling increased the ignition delay times, reduced the maximum flame temperatures, and lowered the production of aluminum monoxide (AlO) radicals compared to traditional aluminum nanoparticles.²

Previous studies of the effects of nitrogen dioxide on the combustion of hydrocarbon fuels were performed in shock tubes, $^{3,6,9,11-13}_{,,5,0}$ flow reactors, $^{4,7,10}_{,,7,10}$ or rapid compression machines⁸ with a vaporized fuel. In experiments and theoretical calculations, the effects of nitrogen dioxide on the combustion were studied for methane (CH_4) , $^{3-13}_{,,5,6,8,10,13,25}$ propane (C_3H_8) , $^{5,25}_{,,5,2}$ and higher molecular weight fuels^{5,25} but not for JP-10. Furthermore, the influence of nitrogen dioxide when ignition is initiated by Al particles has not been investigated. Therefore, we used our ultrasonic levitator apparatus to investigate the effects of nitrogen dioxide on the oxidation of a JP-10 droplet doped with Al nanoparticles while levitated in an oxygen–argon gas mixture. More specifically, we first measured the temperature temporal profiles of the combustion process to determine the effects of



Figure 1. Schematic top view of the levitator apparatus showing (i) the ultrasonic levitator located within the process chamber, (ii) the infrared beamline including the FTIR spectrometer, the first-stage optics, and the IR detector, (iii) the fiber-optic UV–vis spectrometer system, (iv) the Raman spectrometer, (v) the infrared camera, (vi) the droplet deposition system including the syringe, and (vii) the carbon dioxide laser with its mirror optics. The circular inset displays the levitator in more detail viewed from the side.

nitrogen dioxide on the ignition delay times, the initial rate of temperature rise, and the maximum flame temperatures. Second, we collected UV-vis emission spectra during the ignition to identify the radical intermediates, individual atoms, and molecules formed, particularly the radicals associated with nitrogen dioxide. The UV-vis spectra provide valuable information about the effects of nitrogen dioxide on the composition of the radical pool during the oxidation processes. Third, Raman spectra of the droplet were recorded to search for functional groups formed by reaction between nitrogen dioxide and JP-10 before ignition, in which a tightly focused infrared laser beam provided sufficient heating to induce reactions without igniting the droplet. UV-vis reflectance spectra gave complementary information about the interaction between nitrogen dioxide and JP-10 before heating. Fourth, we collected FTIR transmission spectra of the gases formed by the combustion to identify the final state molecules. The combined experimental data provide insight into the effects of nitrogen dioxide on the combustion of a JP-10 droplet with an energy density enhanced by the addition of aluminum particles.

2. EXPERIMENTAL METHODS

The levitator experimental apparatus has been reviewed in detail previously^{26,27} and employed in various experi-ments.^{21,23,24,28–31} A schematic top view of the levitator apparatus illustrating its key components is presented in Figure 1. In the acoustic levitator, ultrasonic sound waves with a frequency of 58 kHz are produced by a piezoelectric transducer and reflect from a concave plate to generate a standing wave (see Figures 1-3). The sound waves produce acoustic radiation pressure,^{32,33} which levitate a sample slightly below one of the pressure minima of the standing wave. The levitator is enclosed within a pressure-compatible process chamber to permit control of the environmental conditions including the ambient gas or gases of interest. For experiments without nitrogen dioxide, the chamber was filled with a 60% oxygen and 40% argon gas mixture at a total pressure of 936 Torr. The nitrogen dioxide increased the instability of the levitated droplet, obscured view of the levitator from outside of the process chamber (Figure 1) for concentrations of about 5% or above, and can damage various components of the experimental apparatus after short exposure. We therefore used the minimum concentration of nitrogen dioxide that produced observable experimental effects. The gas mixtures studied consequently varied from 60% O2, 39% Ar, and 1% NO2 to 60% O2, 35% Ar, and 5% NO2 at a total pressure of 936 Torr (section 3). A droplet was dispensed into the central pressure minimum at 7.5 mm above the transducer plate using a microneedle attached to the end of a wobble stick. The needle is connected via chemically inert polyetheretherketone (PEEK) tubing and then a vacuum compatible valve to a syringe attached to an outside port of the process chamber. A levitated droplet had an oblate spheroidal shape with horizontal and vertical diameters ranging from typically (2.0 \pm 0.1) mm to (2.8 \pm 0.1) mm and (1.2 \pm 0.1) mm to (1.6 \pm 0.1) mm, respectively, where the uncertainties represent the accuracy with which the diameters can be measured using an optical camera. The droplets were ignited or heated by focusing an infrared beam emitted from a carbon dioxide laser with a wavelength of 10.6 μ m to a diameter (1/e²) of 0.2 mm on the droplet, which was performed using a beam expander with a magnification of 8 to minimize the limitation by diffraction followed by a copper parabolic mirror with a focal

length of 300 mm. The duty cycle of the carbon dioxide laser was 80% for all experiments, which produced an output power of 32 W. An optical model describing the propagation of the CO_2 laser beam through a JP-10 droplet containing Al particles was developed in the Supporting Information of ref 21.

In the UV-vis reflectance spectrometer system, the output from a UV-vis source was transmitted by a fiber-optic feedthrough within a conflat flange to seven, 400 μ m illumination fibers of a Y-type reflectance probe inside the process chamber. The fiber-optic probe was aligned on the droplet at a distance of approximately 6 mm using an x, y, zmanipulator. The radiation backscattered from the droplet was collected by a single 600 μ m diameter read fiber, left the chamber via the conflat fiber-optic feedthrough, and finally was dispersed within a StellarNet SILVER-Nova UV-vis spectrometer. The spectrometer is sensitive over the 200 to 1100 nm wavelength range and has a resolution of 2 nm. For UVvis emission spectroscopy, the UV-vis emissions from the igniting droplet were collected by the read fiber. The UV-vis emission spectra were recorded sequentially every 1.7 ms throughout the ignition event.

Raman transitions were excited by the 532 nm line of a diode-pumped, Q-switched Nd:YAG laser.³⁴ A lens with a focal length of 60 mm focused the laser beam onto the sample to form a spot with a diameter $(1/e^2)$ of approximately 20 μ m. The Raman-shifted photons, backscattered from the droplet, were focused by 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 over the Raman-shift ranges of 200-2450 cm⁻¹ and 2400-4000 cm⁻¹ simultaneously. The variation in the sensitivity of the Raman spectrometer with wavenumber can be removed by calibrating with a blackbody source at a temperature of 2700 K. The gases produced by the combustion were identified by collecting an FTIR transmission spectrum in the 400-4000 cm⁻¹ wavenumber region through the full width of the process chamber. The FTIR spectrometer system combines a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with two stages of copper mirror optics.

The method to determine the temperatures during the ignition process has been discussed in detail previously.²⁴ Briefly, infrared thermal imaging videos of the ignition event were recorded using an FLIR A6703sc camera. The camera was set to a frame rate of 387.55 s⁻¹ and observed a 10 mm \times 8 mm field of view (FOV) centered on the droplet. Videos for each ignition were recorded over the temperature ranges of 283-363 K, 353-473 K, 423-623 K, 523-873 K, 773-1473 K, and 973–1773 K of the infrared camera, where the quoted temperatures are before emissivity correction. In each temperature range, the videos were converted to temporal plots of the maximum temperature within the 10 mm \times 8 mm FOV. Finally, the temporal profiles from each of the six temperature ranges were combined to produce one temperature temporal profile over the full range of observed temperatures.

Placing the flame temperature from an infrared camera on an absolute scale requires the emissivity ε of the relevant flame type. To estimate ε , we simultaneously collected a UV-vis emission spectrum and recorded an infrared thermal video of the same ignition process. For a nonblack object at the temperature T with an emissivity of ε , the radiation flux emitted, J, is ε times the radiation flux emitted by a blackbody at the same temperature:^{35,36}

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$$J(\lambda, T, \epsilon) = \epsilon(\lambda, T) \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_{\rm B}T} - 1}$$
(1)

where λ is the wavelength, *h* is Planck's constant, *c* is the speed of light, and $k_{\rm B}$ is Boltzmann's constant. For a so-called gray body, the emissivity ε is independent of the wavelength and temperature. The goodness of the fits using eq 1 with ε constant as a function of the wavelength (see section 3.2) demonstrate that, to a good approximation, the spectra of the flames in the present experiments can be represented by such a gray body. The absolute temperature of the ignition process can be therefore deduced, independently of the emissivity ε , by fitting the gray-body distribution (1) to the background in the UV-vis spectrum. The emissivity in the FLIR ResearchIR Max program was then set to the value that yielded the same temperature as the gray-body source. The resulting value for the emissivity of 0.115 was applied only at temperatures above the autoignition temperature of JP-10, that is, 509 K. The effective pixel size on the levitated droplet at the camerasample distance of 210 mm is 56.5 μ m per pixel. Since at least 10 pixels are required across a sample to accurately determine the temperature, the minimum spatial resolution of the IR camera is approximately 0.6 mm. High-speed optical videos of the combusting droplets were recorded with a Phantom Miro 3a10 camera operating at frame rates of up to 1000 s^{-1} .

The analyte was prepared by mixing 1% by weight of untreated aluminum nanoparticles with JP-10 and then homogenizing the mixture by ultrasonic agitation. The particle-size distribution was measured by dynamic light scattering (DLS) yielding 97 \pm 9 nm. The untreated Al particles were purchased from Novacentrix. For other types of Al nanoparticles studied by alternative experimental techniques, the nanoparticles can separate from the hydrocarbon fuel following ultrasonic agitation. Consequently, some investigators apply surfactants such as oleic acid³⁷ or sorbitane monooleate (Span 80)³⁸ to improve the dispersion of the Al nanoparticles within the fuel. However, when the 100-nmdiameter untreated Al nanoparticles were investigated in the levitator apparatus, the nanoparticles remained well-dispersed within the droplet throughout the experiments without the need for a surfactant. Figure 2 shows a typical example of how the Al nanoparticles were fully dispersed inside the droplet.

3. RESULTS AND DISCUSSION

3.1. Raman Spectroscopy. Photographs of a JP-10 droplet levitated in 1% nitrogen dioxide and 99% argon before and after irradiation by the carbon dioxide laser and interaction with the nitrogen dioxide are shown in Figure 3. To avoid ejecting the droplet from the acoustic trap, the laser irradiation was applied in several bursts lasting approximately 1 s at a duty cycle of 3%. The temperature of the whole droplet, as determined by the infrared camera, increased to about 363 K on each occasion. The localized temperature was much higher, however, in the region of the tightly focused infrared laser beam with a diameter of 0.2 mm, but this temperature could not be measured accurately by the infrared camera owing to limitations in its spatial resolution (section 2). As a result of evaporation and chemical reactions, the JP-10 droplet reduced from 2.4 mm \times 1.5 mm to form a residue with dimensions of 0.8 mm \times 0.5 mm. In contrast, without nitrogen dioxide and heating the JP-10 droplet completely evaporated to leave no levitated product, which confirms that interaction with



Figure 2. Photograph of a levitated droplet of JP-10 containing a 1% concentration of 100-nm-diameter untreated Al nanoparticles. The photograph shows that the nanoparticles were well-dispersed within the droplet, which remained true throughout the duration of the experiments.

nitrogen dioxide and laser irradiation produced new chemical compounds.

For a fluorescent or an amorphous sample, the laser beam with a wavelength of 532 nm is Raman shifted and backscattered to form a spectrum that is continuous across the 200–4000 cm⁻¹ wavenumber range of the Raman spectrometer. The Raman-shift range of 0–4000 cm⁻¹ corresponds to a photon wavelength range of 532–676 nm in which absorption from NO₂ is significant.^{39,40} To determine the effect of absorption by NO₂ on the Raman spectrum, the attenuation A was calculated using

$$A = e^{-n\sigma_{\lambda}l} \tag{2}$$

where *n* is the number density of NO₂ molecules at a concentration of 1% (section 2), *l* is the path length of 18.8 cm for the Raman-shifted laser beam in the process chamber, and σ_{λ} (cm² molecule⁻¹) is the absorption cross section of NO₂ at the wavelength λ .⁴⁰ The resulting absorption spectrum of NO₂ is compared in Figure S1 with a Raman spectrum typical of a JP-10 sample levitated in 1% NO₂ and 99% Ar. Clearly, the structure in the Raman spectrum is dominated by absorption from nitrogen dioxide. In the Raman spectra presented below, we therefore subtracted the nitrogen dioxide absorption spectrum, so that the remaining spectrum was produced only by the levitated sample.

In Figure 4, the Raman spectrum of the residue formed after the processing (top panels) is compared with the spectrum of unreacted JP-10 (bottom panels). In the low Raman-shift range of 2450-240 cm⁻¹, evaporation and reaction with nitrogen dioxide caused the sharp peaks from the pure JP-10 to vanish and multiple new bands to appear superimposed upon a broad, structureless continuum. The total fits (red lines) and individual peak fits (green lines) are included in Figure 4. In fits to the spectrum of the residue, broad underlying peaks



Figure 3. Photographs of a droplet of JP-10 levitated in 1% nitrogen dioxide and 99% argon before (top) and after (bottom) evaporation and irradiation by an infrared laser. Ultrasonic sound waves are generated by the piezoelectric transducer (C) and reflect from the concave plate (A) to generate a standing wave. The horizontal metal cylinder on the left of each photograph (B) is the end of the fiber-optic probe, which was used to collect the UV–vis emission or reflection spectra.

were added in some spectral regions to account for the background or unresolved, overlapping bands. In the high-shift region from $3500-2400 \text{ cm}^{-1}$, the three bands of JP-10 at 2949, 2905, and 2862 cm⁻¹ vanished to be replaced by four bands at 2963, 2931, 2887, and 2849 cm⁻¹ and another new peak appeared at 2729 cm⁻¹. The wavenumbers and assignments for peaks a–g in the JP-10 spectrum before reaction and peaks a–v of the residue are compiled in Tables S1 and 1, respectively.

Raman spectroscopy is a powerful technique to identify the *functional groups* produced by the oxidation. We therefore next consider the organic nitro functional groups that could form by reaction between JP-10 and nitrogen dioxide based on the well-known reactions between hydrocarbon fuels and nitrogen dioxide.⁷ Raman spectroscopy rarely allows individual molecules to be identified, however, except by comparison with the spectrum of a known sample, and the technique does



Figure 4. Raman spectra of a levitated JP-10 droplet after laser irradiation and interaction with NO₂ (black circles) in the (a) 3500–2400 cm⁻¹ and (b) 2450–240 cm⁻¹ Raman-shift ranges (top panel in each figure) compared with the spectra of unreacted JP-10 (bottom panel in each figure). The total fit to the spectra (red lines) and the individual peak fits (green lines) are included. Linear backgrounds have been subtracted from the spectra of the processed sample. The wavenumbers and assignments for peaks a-g in the JP-10 spectrum before reaction and peaks a - v of the residue are compiled in Tables S1 and 1, respectively.

not provide detailed information about the molecular formula or structure.

In the dominant reaction between nitrogen dioxide and a hydrocarbon fuel, NO_2 initially abstracts a hydrogen from the hydrocarbon, RH, to form one of three HNO₂ isomers:^{5,25}

 $RH + NO_2 \rightarrow R + trans-HONO$ (R1)

$$RH + NO_2 \rightarrow R + cis-HONO$$
 (R2)

$$RH + NO_2 \rightarrow R + HNO_2$$
 (R3)

For the example of methane (CH₄), the activation energies E_a for (R1), (R2), and (R3) are 138, 110, and 131 kJ mol⁻¹, respectively.²⁵ These energies E_a for (R1)–(R3) are about 92–121 kJ mol⁻¹ lower than the activation energies required to initiate the ignition with molecular oxygen via RH + O₂ \Rightarrow R + HO₂,⁴ which is one reason why NO₂ enhances the oxidation of hydrocarbon fuels. In Scheme 2, we show the reaction enthalpies, $\Delta H_r(0 \text{ K})$, for the abstraction of atomic hydrogen (H) from each of the six chemically nonequivalent C–H bonds of JP-10 by molecular oxygen (O₂) to form hydrogen peroxide radicals (HO₂). The corresponding reaction en-

Label	Wavenumber (cm ⁻¹)	Functional group or molecule	Region (cm ⁻¹) ^b	Vibrational modes	
a	2963.2 ± 1.0	Methyl -CH ₃	2975 - 2950 m	C-H asym. str.	
b	2930.5 ± 1.0	Methylene -CH ₂ -	2940 - 2915 m-s	C-H asym. str.	
с	2886.5 ± 1.0	Methyl	2885 - 2865 m-s	C-H sym. str. ^c	
d	2849 2 + 1 0	Methylene	2870 - 2840 m-s	C-H sym. str.	
e	2728 5 + 1 2			Combination band or overtone	
f	1610.7 ± 1.2	Organic nitroso, monomers	1625 - 1540 s	N=O str.	
		aliphatic compounds			
		R '0:			
		Organic nitrites, <i>cis</i> -form	1625 - 1610 s	N=O str.	
		R N		secondary $\sim 1615 \text{ cm}^{-1}$	
		<u>`o`</u> ;		tertiary ~ 1610 cm ⁻¹	
		Carbonitrates	1605-1575 s	C=N str.	
		C=NO2 ⁻			
g	1577.3 ± 2.0	Aromatic nitro compounds	1580 - 1485 m-w	asym. NO ₂ str.	
-				-	
		NN SI			
		A-			
		Carbonitrates	1605 - 1575 s	C=N str.	
		Organic nitroso, monomers	1625 - 1540 s	N=O str.	
		aliphatic compounds			
h	1462.1 ± 1.0	Methylene	1480 - 1440 m	Scissor vib.	
i	1443.5 ± 1.0	Methyl	1465 - 1440 m	asym. CH ₃ def. vib.	
j	1365.5 ± 1.3	Methyl	1390 - 1370 w-m	sym. CH ₃ def. vib.	
	1365.5 ± 1.3	Saturated primary and secondary	1385 - 1360 s	sym. NO ₂ str.	
		aliphatic nitro-compounds,			
		CH ₂ -NO ₂ and CH-NO ₂			
		Saturated tertiary aliphatic	1375 - 1340 s	sym NO. str	
		nitro compounds	1575 - 1540 5	sym. NO ₂ su.	
		Aromatic nitro compounds	1370 - 1315 s	sym. NO ₂ str.	
k	1330.5 ± 1.1	Aromatic nitro compounds	1370 - 1315 s	sym. NO ₂ str.	
1	1302.2 ± 1.1	-(CH ₂) _n -	1305 - 1295 s	Twisting vib.	
		Carbonitrates	1315 - 1205 m-w	asym. NO ₂ str.	
		Nitrates -O-NO ₂	1300 - 1250 s	sym. NO ₂ str.	
		Methylene	~1305 w-m	CH ₂ wagging	
m	1156.3 ± 1.1	Aromatic nitro compounds	1180 - 865 m-s	CN str.	
		Carbonitrates	1175 - 1040 s	sym. NO ₂ str.	
n	1065.5 ± 1.2	Aromatic nitro compounds	1180 - 865 m-s	CN str.	
		Carbonitrates	1175 - 1040 s	sym. NO ₂ str.	
		CH ₃ -C (sat. group)	1080 - 960 w	CH ₃ rocking vib.	
0	1034.6 ± 1.2	Aromatic nitro compounds	1180 - 865 m-s	CN str.	
		CH ₃ -C (sat. group)	1080 - 960 w	CH ₃ rocking vib.	
p	968.2 ± 1.1	Methyl C-CH3	~970 w	CH ₃ rocking vib.	
		Saturated primary and secondary	1000 - 915 m-s	CN str., trans-form	
		aliphatic nitro-compounds		,	
		Aromatic nitro compounds	1180 - 865 m-s	CN str.	
q	921.7 ± 1.5	Saturated primary and secondary	1000 - 915 m-s	CN str., <i>trans</i> -form	
		anphatic nitro-compounds	920 850 m c	CN str. gaughe form	
		aliphatic nitro-compounds	720 - 050 III-S	Civ su., guucne- 10fill	
		Aromatic nitro compounds	1180 - 865 m-s	CN str.	
r 831.3 ± 1.1		Aromatic nitro compounds	865 - 830 m-w	NO ₂ def. vib	
		Nitrites, cis-form	850 - 810 m	N-O str.	
s	742.6 ± 1.3	Aromatic nitro compounds	790 - 690 m	NO ₂ def. vib.	
		Nitrates	765 - 745	NO ₂ wagging vib.	
t	(552 - 480) ± 4	Aromatic nitro compounds	590 - 500 w	NO ₂ in-plane bending vib.	
		Nitrates	570 - 500	NO ₂ rocking vib.	
u	423.3 ± 1.2	Alkane	Below 600 cm ⁻¹ m-s	C- C skeletal def. vib.	
v	311.0 ± 1.3	Alkane	Below 600 cm ⁻¹ m-s	C- C skeletal def. vib.	

Table 1. Wavenumbers and Vibrational Mode Assignments⁴¹ for Peaks a-v in the Raman Spectra of the Residue Produced after Levitating Pure JP-10 in 60% O₂, 39% Ar, and 1% NO₂ and Laser Heating^a

^{*a*}The corresponding photographs are presented in Figure 3. ^{*b*}s = strong, m = medium, and w = weak. ^{*c*}Wavenumber increased by electronegative substituents.

thalpies for hydrogen abstraction by NO₂ forming nitrous acid (HNO₂), as shown in Scheme 3, are significantly less endothermic than with molecular oxygen. Therefore, as for the example of CH_4 discussed above, nitrogen dioxide should

enhance the oxidation of JP-10. The reaction rates for (R1)-(R3) and Scheme 3 are, nevertheless, expected to be negligible at room temperature.⁴ Production of the residue suggests that the localized heating provided by the tightly focused infrared

Scheme 2. Abstraction of Atomic Hydrogen (H) from Each of the Six Chemically Non-equivalent C-H Bonds of JP-10 by Molecular Oxygen (O_2) to Form Hydrogen Peroxide Radicals $(HO_2)^{a}$



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

Scheme 3. Abstraction of Atomic Hydrogen (H) from Each of the Six Chemically Non-equivalent C-H Bonds of JP-10 by Nitrogen Dioxide (NO₂) to Form Nitrous Acid Radicals $(HNO_2)^{a}$



^{*a*}The computed reaction enthalpies, $\Delta H_r(0 \text{ K})$, are in units of kJ mol⁻¹.

laser beam (section 2) provided sufficient energy to activate chemical reactions.

The isomers of HONO rapidly dissociate into NO and OH:

$$trans-HONO/cis-HONO \rightarrow NO + OH$$
(R4)

The alkyl group R formed via (R1), (R2), or (R3) can react with NO₂, NO, or O₂ to yield an alkoxy radical (RO), a nitrogroup (RNO₂), a nitroso-group (RNO), or an alkyl peroxyl radical (ROO):

 $R + NO_2 \rightarrow RO + NO$ (R5)

 $R + NO_2 \rightarrow RNO_2 \tag{R6}$

$$R + NO \rightarrow RNO$$
 (R7)

$$R + O_2 \rightarrow ROO$$
 (R8)

The RO radical from (R5) can then react to form a nitrite group (RONO), a nitrate group (RONO₂), or a carbonyl group (R'CHO):

$$RO + NO \rightarrow RONO$$
 (R9)

$$RO + NO_2 \rightarrow RONO_2$$
 (R10)

$$RO + NO_2 \rightarrow R'CHO + HONO$$
 (R11)

$$RO + NO \rightarrow R'CHO + HNO$$
 (R12)

In Table 1,⁴¹ we list the functional groups formed via reactions (R1)-(R12) that produce significant Raman scattering in the wavenumber ranges of the new bands.⁴¹ In the high Ramanshift region of the processed sample shown in Figure 4a, the newly formed bands a-d occur in the 2800-3000 cm⁻¹ range of the alkane C-H stretching modes. Band a at 2963 cm⁻¹ is therefore assigned to an alkane CH₃ asymmetric stretching vibration, whereas the nearby band b at 2931 cm⁻¹ is attributed to a CH₂ asymmetric stretching mode. The symmetric CH₃ and CH₂ stretching modes appear at 2887 cm⁻¹ (band c) and 2849 cm⁻¹ (band d), respectively. In contrast, three bands are observed in the 2800-3000 cm⁻¹ range of JP-10. Bands a and c of JP-10 at 2949 cm^{-1} and 2862 cm⁻¹, respectively, were produced by C-H stretches of the two types of single CH bonds in JP-10 (Scheme 1; Table S1), whereas CH₂ stretching vibrations caused band b at 2905 cm⁻¹. The changes in the spectra after processing evident in Figure 4a therefore suggest that a C–C bond in JP-10 cleaved to produce a CH₂ radical, and then a hydrogen atom migrated or was added to the CH₂ radical moiety to produce a CH₃ functional group.

We next interpret the low Raman-shift region of the processed sample, as shown in Figure 4b. Since the high Raman-shift region was produced by the $-CH_3$ and $-CH_2$ functional groups, modes of $-CH_3$ and $-CH_2$ are also likely to account for some of the observed structure in the low Ramanshift region. Peak f at 1611 cm⁻¹ is assigned to N=O stretches of the organic nitrites or nitroso compounds or both. The small peak g at 1577 cm⁻¹ is attributed to asymmetric stretches of the NO₂ functional group. In contrast to infrared absorption spectra, in Raman spectra the asymmetric NO₂ stretching band is generally considerably less intense than the symmetric NO₂ stretching band, which is consistent with the small amplitude of peak g. The $-CH_2$ - scissor vibration gives rise to peak h at 1462 cm⁻¹, which can barely be resolved from the asymmetric CH₃ deformation vibration band i at 1444 cm⁻¹. The structure from 1370 to 1300 cm⁻¹ includes bands j, k, and l, which were formed by the symmetric CH₃ deformation and the symmetric NO₂ stretching vibrations. The methylene -CH₂ twisting and wagging modes could also contribute in the same spectral region. Bands m-q from 1160 to 920 cm⁻¹ occur in the range of the carbon-nitrogen stretches of the nitro compounds and the CH₃ rocking vibrations. The broad band r around 830 cm⁻¹ and band s at 743 cm⁻¹ could have been produced by NO2 deformation vibrations. Finally, the structure t covering the range from $550-480 \text{ cm}^{-1}$ might be due to the NO₂ rocking or NO₂ in-plane bending vibrations. Thus, in the Raman-shift range of 1610 to 480 cm⁻¹, the new structure is consistent with the formation of organic nitro-functional groups including the nitrite group (RONO), the carbonitrate group $(R^1R^2C=NO_2^{-})$, the nitroso group (RN=O), the aromatic nitro group (ArNO₂), the saturated primary (H_2C = NO₂) and secondary aliphatic nitro-groups ($R^1R^2CHNO_2$), and the nitrate group ($-O-NO_2$). The C=O stretching vibration of the carbonyl functional group (R'CHO) produces Raman bands at wavenumbers around 1700 cm⁻¹. The absence of any significant structure around 1700 cm⁻¹ therefore shows that the carbonyl group was not present in the processed sample in significant quantities.

Adding Al nanoparticles to JP-10 caused the sharp peaks in the Raman spectrum to reduce in amplitude and a large structureless continuum to appear. The reduction in the JP-10 peaks is a consequence of the Al particles absorbing the laser beam, which reduced the path length sampled within the droplet. In contrast to the pure JP-10, no sharp peaks could be observed when the Al-containing JP-10 droplet was levitated in 1% nitrogen dioxide and 99% argon and irradiated with the carbon dioxide laser because, again, the Al nanoparticles caused absorption and a large continuum.

The residue was formed below the ignition temperature of JP-10 and, hence, at significantly lower temperatures than occurred during combustion. Furthermore, the residue was produced over several minutes, which is considerably slower than the ms timescale of the ignition process. We therefore expect that the chain reaction mechanism beginning from (R13) is the dominant mechanism by which NO₂ affects the combustion of JP-10 rather than the production of organic nitro compounds.

3.2. UV-Visible Emission Spectroscopy. The UV-vis emission spectrum produced during the ignition of a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O₂, 35% Ar, and 5% NO₂ is shown in Figure 5. The graybody spectrum and the emission lines were produced within 20 ms of starting the laser irradiation. The combusting droplet remained within the field of view of the fiber-optic probe throughout this emission period. Therefore, the UV-vis spectra were not influenced by the burning droplet later falling out of the trap (see section 3.3). The total fit presented in Figure 5a was obtained by simultaneously optimizing a graybody background and 29 Gaussian peaks across the 270 to 1030 nm wavelength range. The optimized gray-body background enabled the flame temperature to be determined and yielded 2495 \pm 50 K, whereas the fitted Gaussian peaks provided the wavelengths of the emission lines or bands. The same data are presented in Figure 5b except the gray-body background has been subtracted to show the emission lines and bands more clearly. The peak wavelengths or band centers and the assignments for the features labeled a-v in Figure 5b are listed in Table 2.42-45 The UV-vis emission spectra produced by igniting a JP-10 droplet containing untreated Al nanoparticles²¹ or acetonitrile-milled Al nanoparticles²⁴ when levitated in 60% O2 and 40% Ar have been analyzed in detail. The assignments discussed in refs 21 and 24 will be briefly reviewed before the effects of the NO2 on the UV-vis emission spectrum are considered. The OH (A ${}^{2}\Sigma^{+}-X {}^{2}\Pi$) transition produced the most prominent peak in the spectrum at 310 nm.⁴² The $\Delta \nu = 2, 1, 0, \text{ and } -1$ transitions of aluminum monoxide (AlO) (A ${}^{2}\Sigma^{+}$ -X ${}^{2}\Sigma^{+}$) form the four bands centered around 451 nm, 464-471 nm, 486 nm, and 513 nm, respectively, where $\Delta \nu$ denotes the change in the vibrational quantum number ν .⁴² The $\Delta \nu = 1$ or 0 transitions of C₂ (A ${}^{3}\!\Pi_{g}\text{-}X\;{}^{3}\!\Pi_{u})$ also contribute to peaks l and 0 centered at 471 nm and 513 nm, respectively.⁴² Sodium is an impurity often found in all Al particles, which caused the ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ and $^2\mathrm{S}_{1/2}\mathrm{-}^2\mathrm{P}_{1/2}$ unresolved emission doublet at 589 nm. The very



Figure 5. (a) UV-vis emission spectrum produced during ignition of a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O_2 , 35% Ar, and 5% NO_2 . The total fit (red line) was obtained by simultaneously optimizing a gray-body background (blue line) and 29 Gaussian peaks (green lines) across the 270 to 1030 nm wavelength range. (b) The same spectrum as shown in panel a except the gray-body background has been subtracted to display the emission peaks and bands more clearly. The assignments of bands a-v are presented in Table 2.

broad bands between about 600 nm and 900 nm are produced by emissions from water molecules in highly excited vibrational states.⁴⁶ The absorption feature between 900 nm and 1000 nm could be due to the (2, 0, 1)-(0, 0, 0) combination band of the water vapor produced in the combustion (Table 2); however, the optical fiber absorbs in the same spectral range, which complicates the interpretation. The emission lines are produced by chemiluminescence, where the atoms, molecules, or radicals are promoted to electronically excited states via chemical reactions. The chemical reactions providing the energy to promote the electronically excited states together with the reaction energetics are discussed in ref 21 for ignition without NO₂.

To identify the effects of the NO₂, the UV–vis emission spectrum in the 270 to 600 nm wavelength range produced by igniting a JP-10 droplet containing Al nanoparticles when levitated in 60% O₂, 35% Ar, and 5% NO₂ is compared in Figure 6 with the corresponding spectrum for 60% O₂ and 40% Ar. Clearly, the NO₂ produces significant differences in the UV–vis emission spectrum. As a result of adding the NO₂,

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Table 2. Vibrational Mode and Electronic Transition Assignments for the Bands or Peaks in the UV–Vis Emission Spectrum Produced during the Ignition of a JP-10 Droplet Containing Aluminum Nanoparticles When Levitated in 60% O_2 , 35% Ar, and 5% NO_2 or 60% O_2 and 40% Ar (Figures 5 and 6)^{*a*}

peak or band	peak wavelength or band center $(nm)^0$ with NO ₂	peak wavelength or band center $(nm)^b$ without NO_2	molecule, atom, or radical	ref. wavelength (nm)	transition	branch; vibrational quantum numbers: (ν', ν'') or (ν_1', ν_2', ν_3)-($\nu_1'', \nu_2'', \nu_3''$) ⁸
a		289.6	ОН	287.5–289.3 ^c	A $^{2}\Sigma^{+}$ –X $^{2}\Pi$	$R_{1}, R_{2}, Q_{1}, Q_{2}; (2, 1)$
Ь	309.8	308.6	OH	309.0 ^c	A $^{2}\Sigma^{+}$ –X $^{2}\Pi$	Q ₂ ; (0, 0)
			OH	312.2–314.6 ^c	A $^{2}\Sigma^{+}$ -X $^{2}\Pi$	$R_1, R_2, Q_1, Q_2; (1, 1)$
			Al	309.3 ^d	${}^{2}P^{\circ}_{3/2} - {}^{2}D_{5/2}$	
			Al	309.3 ^d	${}^{2}P^{\circ}_{3/2} - {}^{2}D_{3/2}$	
с	318.3		OH	318.5-320.9 ^c	A $^{2}\Sigma^{+}$ –X $^{2}\Pi$	$R_1, R_2, Q_1, Q_2; (2, 2)$
			HCO	318.6 ^c	A_1	
			СН	314.4 ^c	C $^{2}\Sigma^{+}$ –X $^{2}\Pi$	(0, 0)
			NO	319.8 ^c	B $^{2}\Pi$ – X $^{2}\Pi$	(0, 8)
d	337.4	336.7	NH	336.0 ^e	A ${}^{3}\Pi - X {}^{3}\Sigma^{-}$	$Q_{i}(0, 0)$
			НСО	337.6 ^e	A ₁	<i>.</i> .
			O ₂	337.0 ^c	B ${}^{3}\Sigma_{u}^{-}-X {}^{3}\Sigma_{g}^{-}$	(0, 14)
			NO	337.6	B ² II–X ² II	(0, 9)
e	355.4		CN	358.4	$B^{2}\Sigma^{+}-X^{2}\Sigma^{+}$	(3, 2)
c			NO	357.2°	$B^{2}\Pi - X^{2}\Pi$	(0, 10)
t	376.3		NO	378.9	$B^{2}\Pi - X^{2}\Pi$	(0, 11)
g	387.3		CN	387.1	$B^{-}\Sigma^{+} - X^{-}\Sigma^{+}$	(1, 1)
			CN	388.3	$B^{2}\Sigma^{-}X^{2}\Pi$	(0, 0)
h	200.0		ЧСО	387.1 208.4°		K; (0,0)
п	390.0		AL	396.0	A_0 2D $-^2S$	
:	120.7		лі СЧ	421 4 ^c	$r_{3/2} - 3_{1/2}$	$O_{1}(0,0)$
1 i	429.7	452.2		431.4	$A \xrightarrow{2} \Sigma^{+} X \xrightarrow{2} \Sigma^{+}$	(2, 1)
J	451.5	432.5		447.4 451.6 [°]	$A^{2}\Sigma^{+}-X^{2}\Sigma^{+}$	(3, 1)
			AlO	453.8°	$A^{2}\Sigma^{+} - X^{2}\Sigma^{+}$	(7, 2) (5, 3)
k	463.6	464.4	AlO	464.8°	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(1, 0)
1	470.7	471.6	AlO	467.2 ^c	A ${}^{2}\Sigma^{+}$ - a ${}^{2}\Sigma^{+}$	(2, 1)
			AlO	469.5 ^c	A ${}^{2}\Sigma^{+}-a$ ${}^{2}\Sigma^{+}$	(3, 2)
			C_2	469.8 ^{c,e}	$d^{3}\Pi_{a}$ – $a^{3}\Pi_{n}$	(3, 2)
			C_2	471.5 ^{c,e}	$d^{3}\Pi_{\sigma}$ - $a^{3}\Pi_{\mu}$	(2, 1)
			C_2	473.7 ^{c,e}	$d^{3}\Pi_{g}$ – $a^{3}\Pi_{u}$	(1, 0)
m	486.4	485.9	AlO	484.2 ^c	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(0, 0)
			AlO	486.6 ^c	A $^{2}\Sigma^{+}$ –X $^{2}\Sigma^{+}$	(1, 1)
n		491 ± 1	AlO	488.9 ^c	A $^{2}\Sigma^{+}$ -X $^{2}\Sigma^{+}$	(2, 2)
	495 ± 1					
0	513.7	512.9	AlO	507.9 ^c	A $^{2}\Sigma^{+}$ –X $^{2}\Sigma^{+}$	(0, 1)
			AlO	510.2 ^c	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(1, 2)
			AlO	512.3 ^c	A ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$	(2, 3)
			C ₂	512.9 ^{c,e}	$d^{3}\Pi_{g}$ – $a^{3}\Pi_{u}$	(1, 1)
			C_2	516.5 ^{c,e}	$d^{3}\Pi_{g}$ – $a^{3}\Pi_{u}$	(0, 0)
р	588.7	588.9	Na	589.59 ^a	${}^{2}S_{1/2} - {}^{2}P_{3/2}$	
			Na	589.00 ^d	${}^{2}S_{1/2} - {}^{2}P_{1/2}$	
q	671.1	673.7	Al	669.6 ^d	${}^{2}S_{1/2} - {}^{2}P_{3/2}$	
			Al	669.9 ^d	${}^{2}S_{1/2} - {}^{2}P_{1/2}$	
r	698.2	699.7	H_2O	690-710 ^f	ro-vib. mode	(1, 0, 3)-(0, 0, 0)
s	755	754.6	H_2O	712–737 ^f	ro-vib. mode	(3, 0, 1) - (0, 0, 0)
t	784.4		Al	783.5 ^d	$^{2}D_{3/2}-^{2}F_{5/2}$	
			Al	783.6 ^d	${}^{2}D_{5/2} - {}^{2}F_{5/2}$	
			Al	783.6 ^d	$^{2}D_{5/2}-^{2}F_{7/2}$	
u	836 ± 1	843 ± 1	H_2O	811-839 ^f	ro-vib. mode	(2, 1, 1) - (0, 0, 0)
v	931.9	942.1	H_2O	928–966 ^f	ro-vib. mode	(2, 0, 1) - (0, 0, 0)
	945.7					

^{*a*}Emissions from nitrogen-containing radicals are highlighted in bold. ^{*b*}Uncertainties are less than 1 nm unless stated otherwise. ^{*c*}Reference 42. ^{*d*}Reference 43. ^{*b*}Reference 44. ^{*f*}Reference 45. ^{*s*} ν_1 , ν_2 , and ν_3 represent the O–H symmetric stretch, the H–O–H bend, and the O–H asymmetric stretch of H₂O at 2734 nm (3657 cm⁻¹), 6269 nm (1595 cm⁻¹), and 2662 nm (3756 cm⁻¹), respectively.



Figure 6. Comparison between the UV-vis emission spectra in the 270 to 600 nm wavelength range produced during ignition of a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O_2 , 35% Ar, and 5% NO_2 (top panel) or 60% O_2 and 40% Ar (bottom panel). The gray-body backgrounds have been subtracted.

bands c-i appear prominently in the 315-435 nm wavelength range. Bands e, f, g, and possibly c are probably produced by emissions from nitrogen-containing radicals. The NO (B $^{2}\Pi$ -X ² Π) transitions give rise to the so-called β system, which has its strongest bands at 303.5, 319.8, 337.6, 357.2, and 378.9 nm in the present wavelength range.⁴² The NO β -band wavelengths align closely with emission peaks c-f, although the NO emission around 303.5 nm is obscured by the relatively large and broad OH band centered at 310 nm. The NO β -system can be produced by chemiluminescence when O and N atoms recombine. The possible NO emission peaks therefore suggest that some of the NO2 molecules dissociated into their component atoms during the ignition (see (R21) and (R22)) and subsequently recombined. The CN violet system, which is produced by B ${}^{2}\Sigma^{+}-X$ ${}^{2}\Sigma^{+}$ transitions, is well known to occur when hydrocarbon fuels are burned in nitrogencontaining gases such as N2O or air.42 The strongest CN emissions at 358 nm and 387 nm correspond to peaks e and g, respectively. The NH (A ${}^{3}\Pi$ -X ${}^{3}\Sigma^{-}$) transition at 336 nm also produces a strong emission in flames burning in nitrogencontaining gases and could contribute to peak d.⁴² Although not produced by a nitrogen-containing radical, the CH (A $^{2}\Delta$ -X $^{2}\Pi$) emission at 431.5 nm appeared much more prominently when NO2 was present. The strongest peaks of Al in the present wavelength range at 309, 397, 670, and 784 nm⁴⁷ are assigned to peaks b, h, q, and t, respectively, although peak b is mainly produced by the OH transition. Finally, we note that the OH peak around 310 nm is significantly less prominent with the NO_2 .

In summary, as a result of adding nitrogen dioxide the new radicals NO, NH, and CN were produced and the OH band at 310 nm became less prominent. The effects of NO and OH on the combustion of JP-10 are discussed in the reaction model of section 3.3.

3.3. Temperature Temporal Profiles of the Ignition. Infrared thermal imaging videos of an igniting JP-10 droplet doped with a 1% concentration of 100-nm-diameter untreated Al particles initially levitated in 60% O_2 and 40% Ar or 60% O_2 , 35% Ar, and 5% NO₂ are shown in Movies M1 and M2 of

the Supporting Information, respectively. Furthermore, representative infrared thermal images of a JP-10 droplet igniting in 60% O₂ and 40% Ar at 0, 6, and 8 ms after the start of irradiation by the CO₂ laser are presented in Figure 7. Highspeed optical videos of combusting JP-10 droplets doped with Al nanoparticles have been presented in previous publications.²¹ In Figure 8, the temperature temporal profile produced by igniting a JP-10 droplet containing Al nanoparticles initially levitated in 60% O₂, 35% Ar, and 5% NO₂ is compared with the temporal profile for 60% O_2 and 40% Ar. The profiles with and without NO₂ are similar in the early stages of the ignition. Before ignition, the laser irradiation heated the droplet to temperatures just below the autoignition temperature of JP-10 at 509 K after approximately 3 ms. The sharply focused laser beam (section 2) caused the JP-10 to evaporate rapidly and a plume of Al particles to be ejected from the surface of the droplet. An ejected Al particle traversing the carbon dioxide laser beam ignited, which subsequently caused the nearby Al particles and JP-10 vapor to burn. A pure JP-10 droplet did not ignite in the levitator apparatus, partly because the rapid evaporation of a small volume of JP-10 in the region of the laser spot as the temperature approached the boiling point of 458 K caused the remainder of the droplet to cool; in other words, the JP-10 evaporated before it could ignite. The Alejection and ignition mechanism discussed above thus explains why, in contrast to pure JP-10, droplets of JP-10 containing Al particles can be ignited. The ignition delay time, which is defined here as the time to reach the ignition temperature of JP-10 at 509 K, was 3.2 ± 0.1 ms for both profiles. In the Al ignition stage, the temperature rose rapidly and at comparable rates without and with the NO₂, that is, at $(5.1 \pm 0.3) \times 10^5$ K s^{-1} and (4.5 \pm 0.4) \times 10 5 K s^{-1} , respectively. The cloud of combusting Al nanoparticles and JP-10 vapor ignited the whole droplet. The temperature then rose more slowly than during the Al ignition stage and reached a maximum after approximately 15-20 ms. As the fuel was consumed, the temperature started to decrease. Finally, the impulse from the ignition and the high temperature of the surrounding gases



Figure 7. Infrared thermal images of a JP-10 droplet igniting in 60% O_2 and 40% Ar in the (a) 301–307 K, (b) 684–1580 K, and (c) 1421–2273 K temperature ranges at 0, 6, and 8 ms after the start of irradiation by the CO_2 laser, respectively. The color bar on the right of each image gives the temperatures in kelvin.

caused the droplet to escape from the acoustic trap and fall freely onto the transducer plate below after about 50 ms.

The field of view (FOV) of the infrared thermal imaging camera can be aligned to include the full path of the descending droplet and the hottest flames (see section 2). Therefore, the burning droplet remained within the FOV of the infrared camera throughout measurement of the temperature temporal profiles. Furthermore, the maximum temperatures occurred within 20 ms of ignition and, therefore, before the droplet landed on the transducer plate. Thus, measure-



Figure 8. Comparison between the temperature temporal profiles produced by igniting a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O_2 , 35% Ar, and 5% NO_2 or 60% O_2 and 40% Ar. The laser irradiation started at t = 0 ms.

ments of the ignition delay times, the initial rate of temperature rises, and the maximum flame temperatures were all performed before the droplet made contact with the transducer plate and within the FOV of the infrared camera.

To demonstrate the stochastic nature of the combustion process, the temperature temporal profiles in Figure 8 are presented for single ignitions only rather than as smeared-out averages over several ignitions. The differences in the shapes of the profiles with and without NO₂ evident after about 15 ms consequently reflect the stochastic behavior of the flames within the FOV of the infrared camera. To compare the maximum temperatures, $T_{\rm max}$, reached with an improved statistical accuracy, we determined the mean and standard deviation of $T_{\rm max}$ for five ignitions yielding:

 $T_{\rm max}({\rm without \, NO_2}) = 2930 \pm 120 \,{\rm K}$ (3)

$$T_{\rm max}({\rm with \, NO_2}) = 2520 \pm 160 \,{\rm K}$$
 (4)

In summary, (i) the NO₂ produced no measurable differences in the ignition delay times; (ii) the maximum rate of temperature rise, which occurred during the Al ignition stage, was comparable with and without the NO₂; and (iii) the maximum temperature, T_{max} , was higher without the NO₂.

To understand the effects of NO_2 on the combustion, we will briefly review some of the key reactions by which NO_2 affects the combustion of a hydrocarbon fuel. Nitrogen dioxide promotes the oxidation of hydrocarbon fuels by the following reaction mechanism:⁵

 $NO_2 + RH \rightleftharpoons HONO + R$ (R13)

$$HONO \rightleftharpoons NO + OH$$
 (R14)

$$2NO + O_2 \rightleftharpoons 2NO_2 \tag{R15}$$

NO₂ first abstracts a hydrogen from the hydrocarbon, RH, to form *cis*- or *trans*-HONO (R13), as discussed in section 3.1. The HONO isomer then rapidly dissociates into NO and OH (R14). Finally, the NO is converted back into NO₂ by reaction with O₂ (R15) ready for another cycle from (R13) to (R15). The OH radicals produced via (R14) initiate the destruction of the hydrocarbon and, hence, accelerate the ignition. In

addition to reactions (R13)-(R15), NO₂ can promote oxidation of a fuel by converting the radical R, produced via (R13), into a highly reactive alkoxy (RO) radical (R5). RO radicals can also be made when the peroxyl radical (ROO) formed by (R8) reacts with NO:

$$ROO + NO \rightleftharpoons RO + NO_2$$
 (R16)

NO also enhances the oxidation by converting the less reactive hydroperoxyl radical (HO_2) into the highly reactive OH radical:

$$HO_2 + NO \rightleftharpoons NO_2 + OH$$
 (R17)

where the HO₂ was first formed via

$$H + O_2 + M \rightleftharpoons HO_2 + M \tag{R18}$$

Hydroxy radicals OH can also be produced from NO_2 by reaction with H:

$$NO_2 + H \rightleftharpoons NO + OH$$
 (R19)

Thus, reactions (R13)-(R19) predict that NO₂ should significantly reduce the ignition delay times of hydrocarbon fuels, which has been confirmed experimentally and theoret-ically. $^{3,5,6,8-13}$ The ignition delay time depends on experimental conditions such as the fuel type, the temperature, the pressure, the gas composition including the fraction of NO_{24} the type of experimental apparatus employed, and the fueloxidizer equivalence ratio. For example, using a shock tube, Zhang et al. found that adding 1.49% of NO₂ to a CH₄ and Ar gas mixture at a temperature and pressure of 1540 K and 5.0 atm, respectively, caused the ignition delay time to reduce from 1.02 to 0.11 ms.¹³ A similar reduction of order 1 ms was not observed in the present experiments with the Al-containing JP-10 droplets. The different effects of the NO_2 on the ignition delay times for the present experiments and the previous studies is a consequence of each having a different ignition mechanism. For the previous studies without the Al nanoparticles, the nitrogen dioxide promoted the oxidation of the hydrocarbon fuel and, therefore, the ignition via reactions including (R13)-(R19). Conversely, in the present experiments combustion began when an Al nanoparticle was ignited by the CO₂ laser, which was not measurably affected by the addition of the NO_2 for the reasons suggested in section 3.6.

The reaction mechanisms (R13)–(R19) are important in the so-called low-temperature regime where $T \leq 900$ K. In this low-temperature region, the termination route for the H-atom, H + O₂ \rightarrow HO₂, is favored,¹⁰ which explains why NO promotes the oxidation via (R17). In contrast to the chemistry of the ignition process at the relatively low temperatures where (R13)–(R19) are significant, the chemistry is dominated by a chain-branching reaction between H and O₂ at the higher temperatures occurring later in the ignition:¹⁰

$$H + O_2 \rightleftharpoons O + OH$$
 (R20)

The O and OH radicals formed by (R20) promote the oxidation of the hydrocarbon fuel. Since (R20) does not involve nitrogen dioxide or nitric oxide, NO₂ might be expected to have only a minor effect on the radical pool and, hence, on the combustion in the high-temperature oxidation regime including the maximum temperatures, $T_{\rm max}$, reached.¹⁰ However, as temperatures (3) and (4) show, the maximum temperature, $T_{\rm max}$ was lower with the NO₂ by approximately 400 K. Furthermore, in the UV–vis measurements discussed in section 3.2, the OH (A ${}^{2}\Sigma^{+}-X {}^{2}\Pi$) band at 310 nm was

significantly less prominent with NO₂. A lower OH radical concentration caused by NO₂ could contribute toward a reduction in the maximum temperature $T_{\rm max}$.

To suggest a probable explanation for the lower $T_{\rm max}$ with the NO₂, we will discuss the dissociation of NO₂ at increasing temperatures. Nitrogen dioxide decomposes at 420 K into nitric oxide (NO) and oxygen (O₂) via an endothermic reaction:

$$2NO_2 \rightarrow 2NO + O_2, \ \Delta_r H_{gas}(298 \text{ K}) = 114 \text{ kJ mol}^{-1}$$
(R21)

Above temperatures of about 1400 K, the nitric oxide formed by (R21) decomposes into atomic nitrogen (N) and atomic oxygen (O):⁴⁸

$$NO \rightarrow N + O, \Delta_r H_{gas}(298 \text{ K}) = 632 \text{ kJ mol}^{-1}$$
 (R22)

The enthalpy of reaction, $\Delta_r H_{gas}$ for (R22) was calculated at 298 K because $\Delta_r H_{gas}$ is unavailable for atomic oxygen above 298 K.⁴⁹ In contrast to NO₂ and NO, molecular oxygen does not dissociate into atoms (O₂ \rightarrow O + O) significantly below approximately 3000 K. For example, the O₂ dissociation percentages at 2500 K and 2900 K are 0.77 \pm 0.05% and 4.16 \pm 0.20%, respectively.⁵⁰ Therefore, to a good approximation, the effects of O₂ dissociating on the maximum flame temperature T_{max} can be neglected.

To determine the effects of the dissociation reactions (R21) and (R22) on the maximum flame temperature, the specific heat capacity C_p of the combusted gas for a stoichiometric mixture (R23) will be used, that is, 58.1 J mol⁻¹ K. After accounting for the 5% concentration of NO₂, an enthalpy calculation shows that the first step in the decomposition of NO_2 (R21) lowers the maximum temperature T_{max} by 49 K; the second step in the dissociation involving NO (R22) lowers the temperature by 544 K. The total temperature reduction $\Delta T_{\rm max}$ for both dissociations of 590 K is comparable to the observed reduction of 410 K. The slightly lower temperature reduction $\Delta T_{\rm max}$ for the measurements compared to the calculations would occur for an incomplete dissociation of NO₂ and NO, which might happen considering the irregular spatial distributions of the flames and, hence, temperatures. Thus, the thermal dissociation of NO₂ and NO could explain the reduced maximum temperature in the presence of NO₂.

As discussed in section 3.4, FTIR absorption spectroscopy only shows evidence for the usual products of hydrocarbon oxidation, that is CO₂ and H₂O, when NO₂ was present. Therefore, we are justified in using the specific heat capacity C_p of the combusted gas for the stoichiometric mixture (R23), and differences in the specific heat capacities of the final products with or without NO₂ cannot explain the reduction in $T_{\rm max}$. Furthermore, the specific heat capacities C_p of 60% O₂ and 40% Ar compared to 60% O₂, 35% Ar, and 5% NO₂ at 300 K, for example, are 26.0 J mol⁻¹ K and 26.8 J mol⁻¹ K, respectively.⁴⁹ Therefore, differences in the specific heat capacities of the unreacted, ambient gases within the chamber also cannot account for a reduced $T_{\rm max}$.

The infrared camera determines the temperature by measuring the total radiation power in the $3-5 \mu m$ wavelength range, which corresponds to a wavenumber range of $3333-2000 \text{ cm}^{-1}$ where the NO₂ molecule has many intense absorption bands. We determined that absorption by nitrogen dioxide reduces the power reaching the infrared camera by the factor of 0.932 and, hence, the apparent temperature by the

 $T_{\rm max}$ 3.4. Fourier-Transform Infrared Spectroscopy. Figure S2 shows an FTIR absorption spectrum before igniting a JP-10 droplet containing Al particles when levitated in 60% O₂, 39% Ar, and 1% NO₂. The 1% concentration of NO₂ by volume was chosen to maximize the signal without saturating any absorption peaks. The rovibrational bands labeled a-e in Figure S2 are assigned in Table S2 and reveal that NO₂ was in equilibrium with dinitrogen tetroxide $(2NO_2 \Leftrightarrow N_2O_4)$. The FTIR absorption spectrum after igniting the same Alcontaining JP-10 droplet is presented in Figure S3. This FTIR spectrum was collected in transmission mode through the full width of the process chamber a few minutes after the JP-10 had fully oxidized. To show more clearly the newly formed rovibrational bands, the difference between the absorption spectra before and after the ignition is displayed in Figure S4. The new bands labeled a-h in Figure S4 are assigned in Table S3 to modes of CO_2 , ⁵¹ H_2O , ⁴⁹ and unreacted gas-phase JP-10 produced by evaporation.²³ The carbon dioxide and water formed via oxidation of JP-10:

$$C_{10}H_{16}(l) + 14O_2(g) \rightarrow 10CO_2(g) + 8H_2O(g)$$
 (R23)

Thus, FTIR absorption spectroscopy only shows evidence for the usual products of hydrocarbon oxidation, that is, CO_2 and H_2O .

3.5. UV-Visible Reflectance Spectroscopy. In situ UV-vis reflectance spectroscopy in the 200-1100 nm wavelength range provides complementary information about the interaction between the JP-10 droplet and nitrogen dioxide. The UV-vis beam does not induce significant heating and therefore enables the interaction between nitrogen dioxide and IP-10 to be probed at room temperature. The Al nanoparticles significantly reduce the path length sampled by the UV-vis beam and consequently also the amplitude of the absorption features. In this section, we therefore only consider the interaction between nitrogen dioxide and JP-10 without Al nanoparticles. The reflectance R of JP-10 was placed on an absolute scale using its refractive index and the Fresnel equations. The refractive index of JP-10 at 589 nm (sodium Dline) is 1.4877 \pm 0.0003,⁵² which gives a reflectance R of 0.0384 at the same wavelength. The UV-vis reflectance spectrum for a JP-10 droplet levitated in 60% O₂ and 40% Ar is shown in Figure 9. The spectrum has a broad absorption region from 225 nm to 305 nm with minima at 255 nm and 277 nm, which are superimposed on a continuum that rises as the wavelength reduces below 500 nm. The UV-vis reflectance spectrum for levitation in 60% O2, 35% Ar, and 5% NO_2 is included in Figure 9. Thus, the NO_2 reduces the reflectance below around 600 nm and produces a small minimum centered at 340 nm. The change in absorbance A = $\log_{10}(R_0/R)$ caused by the interaction between JP-10 and NO₂ is presented in Figure 10, where R_0 and R denote the reflectance without or with NO2, respectively. The broad absorption peak centered at 340 nm and the continuum that rises as the wavelength reduces are similar to the absorption spectrum of dinitrogen tetroxide (N_2O_4) in the 180–390 nm wavelength range.⁵³ In contrast, the absorbance spectrum in



Figure 9. Comparison between the UV–vis reflection spectra for a JP-10 droplet levitated in 60% O_2 , 35% Ar, and 5% NO_2 or 60% O_2 and 40% Ar.



Figure 10. Absorbance produced by the interaction between a JP-10 droplet and nitrogen dioxide calculated from the reflectance data shown in Figure 9.

Figure 10 does not resemble the absorption from nitrogen dioxide in the same wavelength range.⁵⁴ Therefore, the absorbance presented in Figure 10 could be due to dinitrogen tetroxide dissolved in the droplet. The UV–vis reflectance spectrum shows no evidence for chemical reactions between JP-10 and NO₂, which is as expected at room temperature considering the known activation energies (section 3.1).

3.6. Ignition Reaction Mechanisms for AI-Doped JP-10 Including NO₂. Without NO₂, the AI particles initiate and enhance the combustion by first vaporizing and then forming highly reactive aluminum monoxide (AIO) radicals and atomic oxygen (O) by reacting with molecular oxygen (O_2) :^{21,55}

$$Al_{(gas)} + O_2 \rightarrow AlO + O, \ \Delta H_r(298 \text{ K}) = -14 \text{ kJ mol}^{-1}$$
(R24)

 $\Delta H_{\rm r}$ was calculated at 298 K because the enthalpy of formation, $\Delta_{\rm r} H^{\circ}_{\rm gas}$, is unavailable for atomic oxygen at higher temperatures.⁴⁹ The AlO and O radicals can then abstract atomic hydrogen (H) from each of the six chemically nonequivalent bonds of JP-10 to form aluminum hydroxide

(AlOH) or hydroxyl (OH) radicals, respectively, in mostly endothermic reactions.²¹

AlO +
$$C_{10}H_{16} \rightarrow C_{10}H_{15}$$
 + AlOH,
 $\Delta H_r(0 \text{ K}) = -64 \text{ to } -24 \text{ kJ mol}^{-1}$
(R25)

O + C₁₀H₁₆ → C₁₀H₁₅ + OH,

$$\Delta H_{\rm r}(0 \text{ K}) = -29 \text{ to } +11 \text{ kJ mol}^{-1}$$
(R26)

In contrast, hydrogen abstraction from JP-10 by molecular oxygen is endothermic by up to $236 \text{ kJ} \text{ mol}^{-1}$.

$$O_2 + C_{10}H_{16} \rightarrow C_{10}H_{15} + O_2H,$$

 $\Delta H_r(0 \text{ K}) = 196 \text{ to } 236 \text{ kJ mol}^{-1}$ (R27)

(R24) has no entrance barrier which results in a reaction rate for (R24) that is a factor of 10^9 higher than for direct oxidation by molecular oxygen (R27) at 1000 K.⁵⁵ Therefore, 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.⁵⁵ In addition to the enthalpies of reaction and the energy barriers discussed above, the Al chain mechanism is supported by measurements showing that Al particles increase the combustion efficiencies, the maximum flame temperatures, and the burn times in addition to lowering the ignition delay times (see the Introduction). The steps after (R25) and (R26) in the chain of reactions initiated by Al are detailed in refs 21 and 55.

AlO radicals can also be produced by reaction between gaseous aluminum and nitrogen dioxide:

$$Al_{(gas)} + NO_2 \rightarrow AlO + NO, \Delta H_r(0 \text{ K}) = -206 \text{ kJ mol}^{-1}$$
(R28)

Although the enthalpy of reaction for (R28) is lower than for (R24), enhancement of the combustion by processes not involving NO₂ is expected to remain significant for the following reasons. The energy per mole, $\Delta_{\text{electronic}}$ needed to produce AlO in the A $^{2}\Sigma^{+}$ electronically excited state (Table 2) and, hence, the observed UV–vis emission bands must exceed 246 kJ mol^{-1.21} Therefore, reaction between Al_(gas) and NO₂ (R28) does not provide sufficient energy to produce the AlO emission bands by chemiluminescence observed in the UV–vis spectra. Instead, the AlO (A $^{2}\Sigma^{+}$ –X $^{2}\Sigma^{+}$) bands can be produced by reaction between gaseous aluminum and atomic oxygen:²¹

$$Al_{gas} + O \rightarrow AlO^*, \ \Delta H_r(298 \text{ K}) = -512 \text{ kJ mol}^{-1}$$
(R29)

where * denotes an electronically excited state. Reaction (R28) does not produce highly reactive atomic O, but the O atom required for (R29) can be readily formed via (R24). The conclusion that enhancement of the combustion by processes not involving NO₂ is expected to remain significant is supported by the temperature temporal profiles discussed in section 3.3, where we found that NO₂ did not produce measurable differences in the ignition delay times or the maximum rates of temperature rise.

4. CONCLUSION

An acoustic levitator apparatus was used to investigate the effects of NO_2 on the oxidation of a JP-10 droplet with or without Al nanoparticles. Raman spectra of a JP-10 droplet were collected while levitated in 1% NO_2 and 99% Ar and heated with a carbon dioxide laser. A residue was produced during levitation, which demonstrates that localized heating by the tightly focused infrared laser beam provided sufficient energy to activate chemical reactions between JP-10 and NO_2 without igniting the droplet. Raman spectra of the residue give information about the initial oxidation mechanisms before ignition and suggest that organic nitro compounds formed.

UV-vis emission spectra of an igniting JP-10 droplet containing Al nanoparticles initially levitated in 60% O2, 35% Ar, and 5% NO2 were recorded in the 200 to 1100 nm wavelength range. Emissions from the atoms, molecules, and radicals commonly observed in hydrocarbon flames containing Al were detected, namely, OH, Al, CH, AlO, C₂, and H₂O. The appearance of several Al peaks between 300 nm and 1100 nm and the formation of AlO bands shows that the Al vaporized and subsequently reacted with molecular O₂ or atomic oxygen O. The NO₂ gave rise to additional bands in the 315-435 nm range, which were assigned to CN, NH, and NO radicals. The NO (B ${}^{2}\Pi - X {}^{2}\Pi$) emission bands were produced by chemiluminescence when O and N atoms recombined following the dissociation of NO₂ into its constituent atoms. The OH (A ${}^{2}\Sigma^{+}-X {}^{2}\Pi$) band at 310 nm was significantly less pronounced when NO2 was present, whereas the CH (A $^{2}\Delta$ -X $^{2}\Pi$) band at 432 nm appeared more prominently. The UV-vis emission spectra thus provide important information about the effects of NO2 on the relative abundances of the radicals formed during the ignition process. UV-vis reflectance spectroscopy in the 200 to 1100 nm wavelength range provided complementary information about the interaction between JP-10 and NO₂ at room temperature. The absorbance spectrum following interaction with 5% NO₂ suggests that N_2O_4 dissolved in the droplet, but there was no evidence for chemical reactions between JP-10 and NO₂ without laser irradiation.

We compared the temperature temporal profiles produced by igniting a JP-10 droplet containing Al nanoparticles initially levitated in an oxygen-argon mixture with or without 5% NO₂. The ignition delay time, Δt , measured relative to the start of the laser irradiation, was 3.2 \pm 0.1 ms for both temporal profiles, and therefore the NO2 did not cause measurable differences in Δt . In contrast, the reaction mechanisms without Al particles demonstrate that NO₂ significantly reduces the ignition delay times, which has been confirmed by several experiments and theoretical models (section 3). Similar reductions in Δt were not observed in the present experiments because the ignition mechanisms with and without Al nanoparticles are different; that is, here combustion began when an ejected Al nanoparticle was ignited by the infrared laser beam which is not significantly affected by the presence of NO2. The maximum rate of temperature rise, which occurred during the ignition and burning of the Al nanoparticles, was comparable without or with the NO₂, that is $(5.1 \pm 0.3) \times 10^5$ K s⁻¹ and $(4.5 \pm 0.4) \times 10^5$ K s⁻¹, respectively. However, a 5% concentration of NO₂ lowered the maximum temperature T_{max} from 2930 \pm 120 K to 2520 \pm 160 K, which could be explained by the thermal dissociation of NO₂ and subsequently of NO.

In summary, for a JP-10 droplet containing Al nanoparticles ignited by an infrared laser beam, NO_2 did not produce observable differences in the ignition delay time or the initial rate of temperature rise; however, the maximum temperature reached was lower with the NO_2 . Thus, for the present experimental conditions, NO_2 did not enhance the combustion of JP-10 droplets containing Al nanoparticles in contrast to previous studies without Al.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c10155.

(1) Absorption background from nitrogen dioxide in the Raman spectrum of a levitated droplet; (2) FTIR absorption spectra before and after igniting a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O₂, 39% Ar, and 1% NO₂; (3) Does absorption from nitrogen dioxide reduce the apparent temperature measured by the infrared camera?; Supporting references (PDF)

Infrared thermal imaging video of an igniting JP-10 droplet containing Al nanoparticles with nitrogen dioxide (MP4)

Infrared thermal imaging video of an igniting JP-10 droplet containing Al nanoparticles without nitrogen dioxide (MP4)

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Notes

The authors declare no competing financial interest.

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