**A Combined Spectroscopic and Computational Investigation on the Oxidation of *exo*-Tetrahydrodicyclopentadiene (JP-10; C10H16) Doped with Titanium-Aluminum-Boron Reactive Metal Nanopowder**

Stephen J. Brotton, Sahan D. Perera, Anupam Misra, N. Fabian Kleimeier, Andrew M. Turner, Ralf I. Kaiser\*

*Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

Corresponding Author: ralfk@hawaii.edu

Mark Palenik\*, Matthew T. Finn, Albert Epshteyn\*

*U.S. Naval Research Laboratory, Washington, DC 20375, USA*

Corresponding Authors: [albert.epshteyn@nrl.navy.mil](mailto:albert.epshteyn@nrl.navy.mil)

[mark.palenk@nrl.navy.mil](mailto:mark.palenk@nrl.navy.mil)

Bing-Jian Sun, Li-Jie Zhang, Agnes H. H. Chang\*

*Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan*

Corresponding Author: [hhchang@gms.ndhu.edu.tw](mailto:hhchang@gms.ndhu.edu.tw)

**ABSTRACT**

We report results on the combustion of single, levitated droplets of *exo*-tetrahydro­dicyclo­pentadiene (JP-10) doped with titanium-aluminum-boron (Ti-Al-B) reactive metal nanopowders (RMNPs) in an oxygen (60 %) – argon (40 %) atmosphere exploiting an ultrasonic levitator with droplets ignited by a carbon dioxide laser. UV-Vis emission spectroscopy revealed the presence of gas phase aluminum (Al) and titanium (Ti) atoms. These atoms can be oxidized in the gas phase by molecular oxygen to form spectroscopically detected aluminum monoxide (AlO) and titanium monoxide (TiO) transients. Analysis of the optical ignition videos supports that the nanoparticles are ignited before JP-10. The detection of boron monoxide (BO) proposes further an active surface chemistry through oxidation of the RMNPs and the release of at least boron monoxide (BO) into the gas phase. The oxidation of gas phase boron monoxide (BO) by molecular oxygen to boron dioxide (BO2) plus atomic oxygen might operate in the gas phase, although an involvement of surface oxidation processes of RMNPs to boron dioxide (BO2) cannot be discounted. The UV-Vis emission spectra revealed also key reactive intermediates (OH, CH, C2, HCO) of the oxidation of JP-10. Electronic structure calculations reveal that the presence of reactive radicals has a profound impact on the oxidation of JP-10. Whereas titanium monoxide (TiO) reacts to produce titanium dioxide (TiO2), it does not engage in an active JP-10 chemistry as all abstraction pathways are endoergic by more than 217 kJ mol-1. This is similar for atomic aluminum and titanium, whose hydrogen abstraction reactions from JP-10 were revealed to be endoergic by at least 77 kJ mol-1. Therefore, aluminum and titanium react preferentially with molecular oxygen to their monoxides. However, the formation of boron monoxide (BO), aluminum monoxide (AlO), and boron dioxide (BO2) supplies a pool of highly reactive radicals, which can abstract hydrogen from JP-10 via transition states ranging in only 1 to 5 kJ mol-1 above the separated reactants forming JP-10 radicals along with the hydrogen abstraction products (HBO, AlOH, HOBO) in overall exoergic reactions. These abstraction barriers are well below the barriers of abstractions for ground state atomic oxygen and molecular oxygen. In this sense, gas phase boron monoxide (BO), aluminum monoxide (AlO), and boron dioxide (BO2) catalyze the oxidation of gas phase JP-10 via hydrogen abstraction forming highly reactive JP-10 radicals. Overall, the addition of RMNPs to JP-10 does not only provide a higher energy density fuel, but is expected to lead to shorter ignition delays compared to pure JP-10 due to a highly reactive pool of radicals (BO, AlO, BO2) formed in the initial stage of the oxidation process.

**1. Introduction**

Contemporary combustion processes in air-breathing propulsion systems rely on the oxide­tion of hydrocarbon-based fuel such as of Jet Propellant-10 (JP-10). *Exo*-tetra­hydrodicyclopentadiene (C10H16; Figure 1) represents a single component hydrocarbon fuel and is the dominant constituent of JP-10 as exploited in detonation engines, missiles, and supersonic combustion ramjets.[1-4](#_ENREF_1) With attractive properties such as a high thermal stability and volumetric energy density of close to 40 kJ cm-3 when completely oxidized, JP-10 has drawn extensive attention from the experimental, theoretical, and modeling communities[5-41](#_ENREF_5) to examine the features of thermal decomposition and the mechanisms of oxidation. Exploiting shock tubes,[37](#_ENREF_37) flow tubes,[7-8](#_ENREF_7), [17-18](#_ENREF_17) and high temperature chemical reactors,[9-10](#_ENREF_9), [13](#_ENREF_13), [16](#_ENREF_16) a detailed understanding of the *decom-position* (pyrolysis) of JP-10 is beginning to emerge. This unimolecular decomposition leads to smaller C2-C9 hydrocarbon molecules and reactive transient species, among them aliphatic radicals, resonantly stabilized free radicals (RSFRs), and aromatic radicals (ARs),[42](#_ENREF_42) which *initiate* and *drive* the complex chemistry in the oxidation of JP-10 based jet fuel. This initial decomposition chemistry, [43](#_ENREF_43) which has been suggested to be temporarily uncoupled from the oxidation stage at least in the absence of metal catalysts,[44](#_ENREF_44) is often dubbed as *delivering the building blocks* for the oxidation of JP-10.

However, concerns on the limited volumetric energy density of traditional hydrocarbon fuel of only up to 40 kJ cm-3, which severely constrains the range and hence performance of air-breathing propulsion systems, are growing. The development of the next generation of air-breathing propulsion systems requires fuel with higher energy per volume and molecular weight compared to traditional hydrocarbon fuel. This necessitates the development of the next generation of high energy density fuels and of high energy density fuel additives [45-51](#_ENREF_45) ultimately enhancing the performance and range of air-breathing propulsion systems. High energy density fuel additives based on reactive metal nanopowders (RMNPs) hold promise in air breathing engine applications. However, there is currently an incomplete understanding of the underlying elementary mecha­ni­sms involved in the oxidation of RMNPs-doped hydrocarbon-based fuel such as JP-10. Boron holds the highest energy density of 138 kJ cm-3 compared to other combustible metals such as aluminum (84 kJ cm−3) or magnesium (43 kJ cm−3). However, the refractory nature of boron, which is reflected in high melting and boiling points of 2,349 K and 4,200 K, respectively, makes it difficult to ignite and prevents it from gasification during combustion. The RMNPs are a demonstration of an approach to harness boron combustion, where boron is mixed with reactive metals such as titanium and aluminum, providing more favorable combustion characteristics. Titanium and aluminum undergo exoergic reactions with boron forming borides such as aluminum diboride (AlB2) and titanium diboride (TiB2).[52-54](#_ENREF_52) This has the potential to heat up the RMNPs to tempe­ra­tu­res at which boron oxidation can readily occur thus relieving the complications of kinetic trap­ping of boron as metaboric acid (HOBO), which prevents the full energy release. Therefore, RMNPs containing titanium, aluminum, and boron represent a new classes of high energy density fuel additives with a volumetric energy content exceeding 89 kJ cm-3. Epshteyn et al. proposed RMNPs prepared through sonochemically mediated dehydrogenation of *in situ* generated complex metal hydrides[55](#_ENREF_55) as promising fuel additives due to their high specific surface area, high energy density, and potential catalytic capability.[52-54](#_ENREF_52), [56-60](#_ENREF_56) The authors demonstrated that newly developed RMNPs containing titanium (Ti), aluminum (Al), and boron (B) in JP-5 at concentrations of up to 4 % by weight resulted in shorter ignition delays of the hydrocarbon, i.e. the period between the beginning of fuel injection into an engine cylinder and the beginning of combustion, and increased burn durations.[61](#_ENREF_61) The RMNPs additives resulted in an increase of nitrogen oxides, carbon dioxide, and carbon monoxide and simultaneous oxygen decrease in the exhaust compared to results with pure JP-5 as a reference system. As revealed in combustion studies of RMNPs in decane liquid fuel spray burners,[57](#_ENREF_57), [61](#_ENREF_61) the exploitation of RMNPs overcomes traditional problems encountered with metal nanoparticles, i.e. a passivation layer of oxides that reduces the active metal content since the oxide shell becomes an increasing portion of the overall fuel mass as particle size is reduced, which in turn has the potential to significantly increase the overall volumetric energy density of the fuel.[45](#_ENREF_45), [62-64](#_ENREF_62)

However, the underlying mechanisms in the oxidation of mixed, multi-metal RMNPs have not been comprehensively unraveled to date. Considering this lack of detailed knowledge, the objectives of the present work are to investigate the oxidation of acoustically levitated droplets of JP-10 doped with 2 wt % titanium (Ti)-aluminum (Al)-and boron (B)-based RMNPs (system a) in an atmosphere of 60 % oxygen and 40 % argon with the oxidation initiated by a carbon-dioxide laser. It shall be stressed that under these conditions, droplets of pure JP-10 in the absence of metal powder additives did not ignite, but instead evaporated prior to their ignition.[65](#_ENREF_65) We also explore the effects of adding 1 wt % surfactant (Span®80) to the JP-10-RMNP droplet (system b) on the oxidation process including, e.g., ignition delay and maximum flame temperature. JP-10 droplets doped with 2 wt % aluminum (Al) (system c) and 2 wt % aluminum (Al) along with 1 wt % surfactant (Span®80) (system d) serve as baseline systems to determine the improvements in the combustion compared to the more traditional single-metal additive Al and investigate the effects of the sorbitane monooleate.[65-68](#_ENREF_65) These experiments are complemented by electronic structure calculations exploring the initial steps on the formation of JP-10 based hydrocarbon radicals accessed through hydrogen abstraction pathways by molecular oxygen (O2, X3Σ−g), atomic oxygen (O(3Pj)), and oxides (BO(X2Σ+); AlO(X2Σ+); TiO(X3Δ); BO2(X2Σg+)) formed during the oxidation of the RMNPs to gauge the effect of Ti-Al-B-based RMNPs on the oxidation of JP-10.

**2. Experimental Methods**

**2.1. Materials**

JP-10 (C10H16, ≥ 98%), the sorbitane monooleate surfactant (C24H44O6-Span® 80) (Figure 1), and aluminum nanoparticles (AlNPs) with diameters of 251 ± 36 nm were purchased from BOC Science, Sigma Aldrich, and Novacentric, respectively. The RMNPs were synthesized in house via the previously published procedure utilizing a sonochemically-mediated decomposition of unstable mixed-metal hydrides of Ti, Al, and B generated in situ; the specific procedure involved the “reverse” addition with a thermal vacuum treatment performed at 373 K, but the reaction was performed on approximately a three-fold increased scale.[55](#_ENREF_55) The resultant RMNPs were found to exhibit an average particle size of 160 ± 80 nm as determined via dynamic light scattering with a Ti:Al:B atomic ratio of approximately 1:2:6. Two distinct RMNPs-loaded JP-10 samples were prepared by mixing JP-10 with (a) 2 wt % of Ti-Al-B-based RMNPs (JP-10-RMNPs) and with (b) 2 wt % of Ti-Al-B-based RMNPs along with 1 wt % of Span®80 (JP-10-RMNPs-surfactant). We also prepared two reference systems of JP-10 samples by mixing JP-10 with (c) 2 wt % aluminum (Al) (JP-10-Al) and (d) 2 wt % aluminum (Al) with 1 wt % surfactant (Span®80) (JP-10-Al-surfactant). Without the surfactant, the RMNPs did not disperse uniformly within JP-10. However, the addition of the surfactant essentially eliminated particle agglomeration, and the RMNPs were uniformly dispersed and suspended in JP-10. The samples were sonicated using a benchtop ultrasonic cleaning bath (Branson 3510:115 V AC, 10 min) immediately prior to each experiment to ensure that no separation between the particles and the liquid takes place during the experiments.

**2.2. Acoustic Levitation Apparatus and Characterization Techniques**

       The oxidation process for single, levitated JP-10 droplets doped with Ti-Al-B-based RMNPs (hereafter: Ti-Al-B-RMNPs) was explored experimentally utilizing an ultrasonic levitation device as described in References [66](#_ENREF_66), [69-71](#_ENREF_69) in detail. Briefly, the core of the levitator comprises a piezo­electric transducer operating at an oscillation frequency of 58 kHz along with a concave shape reflector. In a gaseous medium, a standing wave is generated through the reflection of the ultrasonic soundwaves between the transducer and the reflector. The acoustic radiation pressure counter-balances the gravitational force and therefore levitates the droplet slightly below one of the pressure minima of the standing wave. The ultrasonic levitator is housed in a pressure-compatible stainless steel process chamber, which enables the levitated droplet to be studied in distinct gas(eous) environments (inert, toxic, and/or reactive) over a pressure range from a few 10s Torr up to 1,500 Torr, although in principle higher operational pressures are sustainable. Here, droplets were levitated in an environment of 60 % oxygen (O2, 99.9999 %, Airgas) and 40 % argon (Ar, 99.9999 %, Airgas) at a total pressure of 860 ± 1 Torr. The droplets were oblate spheroids with average horizontal and vertical diameters of 2.6 ± 0.2 mm and a mean vertical diameter of 1.4 ± 0.2 mm, respectively, leading to typical droplet volume of 5 ± 1 mm3, where the uncertainties represent how accurately we could control the size of the droplets for repeated droplet depositions. The droplets were injected into the pressure node through a home-made droplet deposition system comprising a micro needle, a wobble stick, polyetheretherketones (PEEK) tubing, which connects the needle to a syringe located on the outside of the process chamber. After the stabilization of the droplet, levitated droplets of systems (a) and (b) as defined in section 2. were then heated by the output of a carbon dioxide (CO2) laser emitting at a wavelength of 10.6 µm. A planar copper mirror and zinc selenide (ZnSe) windows on the chamber are used to transport the infrared beam to the levitated particle, which is located 104 cm from the exit of the laser as measured along the path of the beam. The diameter of the beam exiting the laser is 2.5 ± 0.5 mm (1/e2) and the beam divergence (full angle) less than 7.0 mR. By using a 8× beam expander followed by a copper parabolic mirror with a focal length of 300 mm, the laser beam was focused to a diameter of 0.2 mm on the droplet.[66](#_ENREF_66), [69](#_ENREF_69) The laser output can be tuned in between 1W to 40W; the present experiments were conducted at an output power of 32 W, which was achieved by setting the duty cycle of the laser to 80 %[.](#_ENREF_48)

     Prior to the ignition, the doped JP-10 droplets were characterized spectroscopically via Raman and Fourier Transform Infrared Spectroscopy (FTIR).[65-66](#_ENREF_65), [69](#_ENREF_69) Raman transitions were excited by the 532 nm line of a diode-pumped, Q-switched Nd:YAG laser (CrystaLaser; Model QL532-1W).

The penetration depth δ of the laser is defined as the power the light decreases to 1/e of its value; this can be calculated via δ= λ / 4πκ where λ is the wavelength of the light (532 nm) and κ is the imaginary part of the complex refractive index of the material. For JP-10, κ is 1.48 for 532 nm. This gives a penetration depth of the Raman diagnostic of 29 nm.

At a typical pulse repetition rate of 1 kHz, the average power output was 200 mW and the pulse width 13.5 ns. The laser beam was directed into the chamber through an anti-reflection coated window after deflection from a 45° mirror (Edmund Optics; Model NT45-991, > 99% reflectance) and a 45° dichroic beam splitter (Semrock; RazorEdge, Model LPD01-532RU-25 × 36 × 2.0). A plano-convex lens with a focal length of 60 mm focuses the laser beam onto the sample and subsequently collimates Raman-shifted photons which were backscattered from the levitated droplet. Although the dichroic beam splitter reflected the incident 532 nm laser beam toward the sample, it transmits the longer Raman-shifted wavelengths of the backscattered photons. After passing through a 532 nm RazorEdge® ultrasteep long-pass edge filter (Semrock; Model LP03-532RE-25), which further minimizes the elastically scattered 532 nm laser light, a 50 mm f/1.8 camera lens (Nikon; Nikkor 2137) focuses the backscattered beam through the entrance slit of the spectrograph. The slit width of 100 μm results in a wavenumber resolution of 9 cm−1. The light then enters a Holospec f/1.8 imaging spectrometer (Kaiser optical systems; Model 2004500-501), where the diverging beam is collimated by a lens towards two overlaid holographic transmission gratings (Kaiser Optical Systems; Model Holoplex HPG-532). One grating disperses the low Raman-shift wavenumbers from 2388 to 168 cm−1, whereas the other separates the higher Raman-shifts in the 4387–2265 cm−1 range. The gratings simultaneously disperse light from the two Raman-shift ranges onto spatially distinct halves of a Peltier-cooled charge-coupled device (CCD) detector kept at 255 K (Princeton Instruments, PI-MAX2), which is composed of 1024 × 256 pixels each with pixel size of 26 μm.

     To reduce the fluorescent background and enable spectra to be collected in bright light conditions, the pulsed laser described above and a gated detector are employed. To detect the faster Raman signal whilst rejecting most of the longer-lived fluorescence, we optimized the time delay between the laser pulse and opening the gate to collect the CCD signal (gate delay) and the period for which the gate is open (period). In the present setup, the CCD is open for 50 ns with a gate delay of 480 ns (T = T0 + 480 ns). The repetition rate of the above procedure was controlled by a Quantum Composers (Model 9518+) pulse generator, which produced 1 μs wide TTL outputs from its channels A and B to trigger the CCD controller and laser, respectively, at a rate adjustable between approximately 100 Hz and 8 kHz.[72](#_ENREF_72) Peak assignments were based on scaled compu­tational normal modes of JP-10 (Figure S7).[73](#_ENREF_73) The Raman-shift scale was calibrated using cyclohexane, toluene, and acetonitrile as described in the Supplementary Information (Figure S8).

     The ignition and oxidation processes of JP-10 in the presence of RMNPs (system a) and RMNPs-surfactant (system b) were characterized exploiting Ultraviolet-Visible (UV-Vis) and Fourier-Transform Infrared (FTIR) spectroscopies along with a high-speed optical and an IR thermal-imaging and camera. UV−Vis emission spectra of the flames were collected to identify the radical intermediates, individual atoms, and molecules formed *during* the oxidation processes, whereas the FTIR transmission spectra of the gases produced *after* the combustion were recorded to identify the terminal oxidation products. The UV-Vis spectra were recorded using a StellarNet SILVER-Nova UV-Vis spectrometer combined with a fiber-optic probe. The fiber-optic probe was aligned on the droplet at a distance of approximately 6 mm using an x, y, z manipulator. For UV-Vis *emission* spectroscopy, the UV-Vis emissions from the igniting droplet were collected by the read fiber, exited the chamber via a conflat fiber-optic feedthrough, and finally were dispersed within the UV-Vis spectrometer, which is sensitive over a wavelength range from 200 to 1,100 nm and has a spectral resolution of 2 nm. FTIR transmission spectra were collected with the help of a Nicolet 6700 FTIR spectrometer over the wavelength range of 500-5,000 cm-1 with two stages of copper mirror optics to probe gases evolved during the ignition event.

     Optical videos of these high-speed ignition events were captured by a Phantom Miro 3a10 camera (Supporting Information; Movies M1 and M2) equipped with a Navitar Zoom 6000 modular lens system at a rate of 1 kHz. Additionally, thermal-imaging videos of the ignition process were collected by an FLIR A6703sc infrared camera, which were converted to temporal plots of the maximum temperature within the 10 mm × 8 mm field of view (FOV). The temperature temporal profiles enable some of key features of the combustion process to be examined; for example, the ignition delay time, the maximum flame temperature (Tmax), and the burn rates. The emissivity of the flames ε is required to place the uncalibrated temperatures from the IR camera on an absolute scale. The emissivity was deduced by fitting a grey-body distribution to the background in the UV−Vis spectrum and then comparing the resulting absolute temperature with the uncalibrated value obtained from an infrared thermal video of the same ignition process. 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.

**3. Computational Methods**

    Reaction energetics involving the atoms (B, Al, Ti) and oxides (BO, AlO, TiO, BO2) were computed in Gaussian09[74](#_ENREF_74) with spin-projected MP2[75](#_ENREF_75) and the 6-311g\* basis set.[76-78](#_ENREF_76) For comparison, reaction, product, and transition state energies for hydrogen abstraction from JP-10 to AlO were computed at a single site using MP2 with the larger def2-TZVP[79](#_ENREF_79) basis set, which did not result in significantly different relative energies or geometries. Overall reaction energies for hydrogen abstraction to the atoms and oxides were also computed using density functional theory (DFT) with the B3LYP[80-82](#_ENREF_80) functional, including Grimme’s D3 [83](#_ENREF_83) emprirical dispersion correction, and the def2-TZVP basis set (B3LYP-D\*/def2-TZVP). Various trial structures for JP-10 were built by hand and optimized to an energy minimum. The lowest energy structure after optimization was used as the starting point for all subsequent calculations. In most reactions, stable, noncovalently bound van-der-Waals complexes occurred on either side of the transition state. To find these comples, a series of trial structures were generated, optimized to an energy minimum, and discarded if they did not converge to a relevant geometry. Initial estimates for transition states were generated from these noncovalently bound intermediates using the geometric velocity method [84](#_ENREF_84) and refined with a combination of saddle-point [85](#_ENREF_85) and synchronous transit-guided quasi-Newton [86-87](#_ENREF_86) optimizations. Our attempts to model hydrogen abstraction to metal-containing complexes with DFT in the def2-TZVP basis set found that both the B3LYP and PBE [88-89](#_ENREF_88) functionals significantly underestimated the transition state barriers; adding a D3 empirical dispersion correction did not remedy this. The use of MP2, which is well-suited to capturing dynamical electron-correlation effects, remedied both of these problems. Energies for carbon-hydrogen bond cleavages in JP-10 leading to six distinct hydrocarbon radicals R1 to R6 (Figure 2) were computed using MP2/6-311g\* B3LYP-D\*/def2-TZVP. These values were compared to previous calculations at the B3LYP/6-311G\*\* and G3 levels (Table 1).[42](#_ENREF_42) Deviations between the B3LYP-D\*/def2-TZVP results and both sets of previous calculations are less than 5 kJ mol-1. The small discrepancies with the previous B3LYP calculations are likely due to the fact that the present work uses a significantly larger basis. Additionally, the previous work did not include an empirical dispersion correction, although this should have had a minimal impact on hydrogen abstraction energies due to the lack of non-covalent interactions.

     The reactions of O (3P) + JP-10 🡪 JP-10 radicals (R1-R6) + OH and O2 + JP-10 🡪 JP-10 radicals (R1-R6) + O2H were explored on adiabatic triplet ground-state potential surfaces. The transition states that lead to van-der-Waals complexes in the exit channels and products, JP-10 radicals and OH, or O2H are identified and characterized utilizing B3LYP [80-81](#_ENREF_80), [90-91](#_ENREF_90)/cc-pVTZ calculations to obtain optimized geometries and harmonic vibrational frequencies, except for R2(TS), R4(TS), R2-OOH, and R4-OOH, which were located at the MP2/cc-pVDZ level of theory. Their energies are further refined at the CCSD[92-95](#_ENREF_92) /cc-pVTZ level of theory with B3LYP/cc-pVTZ zero-point energy corrections. The GAUSSIAN16 program [96](#_ENREF_96) was employed in the electronic structure calculations.

**4.   Results & Discussion**

**4.1. Raman and FTIR Spectroscopy**

       The Raman and FTIR spectra of pure JP-10 are dominated by fundamental modes of the JP-10 molecule covering CH/CH2 stretching modes (2,865–2,954 cm-1), CH2 scissor modes (1,444-1,463 cm-1), CH/CH2 rocking, bending, twisting, and wagging modes (1,030-1,420 cm-1), carbon-carbon stretching, rocking, and bending modes (188-980 cm-1), and ring twisting, rocking, and stretching (Figures S3-S10; Table S1). Upon addition of aluminum nanoparticles, the peaks shift only by 2 cm-1 at most; this is within the resolution of the Raman spectra. However, the addition of the JP-10-Ti-Al-B NPs changed the Raman spectra in various aspects. *First*, as evident from Table S1, various fundamentals are red-shifted by up to 14 cm-1 due to the intermolecular forces between the JP-10 molecules and the surfaces of the Ti-Al-B NPs. *Second*, the υ10 mode, which is Raman inactive, becomes Raman active in the JP-10-Ti-Al-B NP system. *Third*, two additional peaks at 227 cm-1 (νA) and 267 cm-1 (νB) can be linked to Al-B and Ti-B stretching modes of aluminum borides and titanium borides, which were also observed in the pure Ti-Al-B NPs (Figures S3-S8).[73](#_ENREF_73), [97-109](#_ENREF_97)We did not detect any evidence of features associated with titanium-aluminides. This might due to the fact that titanium and aluminum resemble less prominent components of the boron-dominated RMNPs (Ti:Al:B = 1:2:6) or that Ti and Al forms stronger bonds with boron.

It shall be highlighted that in order to record Raman spectra, the 532 nm laser beam, which has a diameter of about 2.5 mm at the 60 mm lens inside the recipient, shall be unfocussed; in other words, the 532 nm laser beam has to pass through the 3 mm hole of the lens. Passing the laser beam through a lens without a hole results in a 45–50 µm laser spot size onto the droplet. This leads to a photochemical activation of the JP-10 by the Ti-Al-B NPs. This photochemical processing results in five new Raman peaks υL1 to υL5 (Figure S11). The low frequency modes at 293 cm-1 (νL1) and 420 cm-1 (νL2) could be attributed to prominent Ti-C and AL-C stretching modes observed in the literature for titanium carbides at, e.g., 425 cm-1. The higher frequency modes at 1,838 cm-1 (νL3), 1,977 cm-1 (νL4), and 2,127 cm-1 (νL5) are likely linked to Al-H (νL3, νL4) and B-H stretching modes (νL5). Ti-H stretching modes are expected to arise in the range of 1,400 – 1,600 cm-1, but could not be assigned unambiguously. Nevertheless, these new features formed upon exposing Ti-Al-B NPs doped JP-10 to focused 532 nm light reveal an active photochemistry at 532 nm.[107-117](#_ENREF_107)

**4.2 Temperature Profiles**

      Figures 3-6 display the temperature profiles for the ignition of JP-10 droplets in the presence of: (a) 2 wt % Ti-Al-B RMNPs (hereafter: Ti-Al-B RMNPs), (b) 2 wt % Ti-Al-B RMNPs – 1 wt % surfactant (hereafter: Ti-Al-B RMNPs - surfactant), (c) 2 wt % Al NPs (hereafter: Al NPs), and (d) 2 wt % Al NPs – 1 wt % surfactant (hereafter: Al NPs - surfactant). The complete combustion process of droplets takes typically 100 – 150 ms. However, after about 40 ms, the system becomes unstable due to mass loss, and the droplet falls out of the trap since the resonance conditions are not met. These profiles reveal interesting findings. *First*, the temperature temporal profiles produced by igniting a JP-10 droplet containing 200 nm diameter Al particles (sample d) or 160 nm-diameter Ti-Al-B particles (sample b) are compared (Figure 3). To help ensure that we investigated the effects of the different chemical compositions of samples (b) and (d) rather than how these particles were homogenized throughout the JP-10, both types of particle were coated in the surfactant. No statistically significant differ­rences in the ignition delay time, Δt, or the maximum rate of temperature rise, dT/dtmax were observed, that is Δt (Ti-Al-B RMNPs - surfactant) = 0.8 ± 0.2 ms, Δt (Al NPs - surfactant) = 0.6 ± 0.2 ms, dT/dtmax (Ti-Al-B RMNPs - surfactant) = (2.5 ± 0.3) × 105 Ks-1, and dT/dtmax (Al NPs - surfactant) = (2.3 ± 0.3) × 105 Ks-1, where Δt is defined as the time to reach the ignition temperature of JP-10 at 509 K. However, the maximum flame temperature, Tm, which was attained after typically 20 to 35 ms, was likely lower for the Ti-Al-B particles, that is Tm (Al NPs - surfactant) = 2870 ± 280 K versus Tm (Ti-Al-B RMNPs - surfactant) = 2550 ± 280 K. Furthermore, the probability of igniting the Al NPs was higher than for the Ti-Al-B RMNPs, since the ignition percentages were 100 % and 64 %, respectively. This could be due to the higher barrier of oxidation of the RMNPs compared to aluminum nanoparticles.[54](#_ENREF_54)

*Second*, to investigate the effects of the surfactant on the ignition delay time and the maximum flame temperature, in Figures 4 – 6 we compared the temperature temporal profiles produced by igniting a JP-10 droplet containing Ti-Al-B RMNPs and Al-NPs with and without the surfactant. The surfactant significantly reduced the ignition delay time from 10 ms to less than 0.5 ms, although it did not significantly affect the rate of temperature rise. The surfactant reduced the ignition delay time by helping to disperse the particles uniformly throughout the JP-10, which increases the probability that a particle will enter the path of the laser beam and, hence, be ignited (section 4.3). As expected from the small amount of surfactant molecules in the solution, the maximum flame temperatures are identical within the experimental errors: Tm (Ti-Al-B RMNPs - surfactant) = 2550 ± 280 K versus Tm (Ti-Al-B RMNPs) = 2410 ± 340 K. Furthermore, the surfactant increased the probability of ignition from approximately 37 % to 64 %. To compare the maximum temperatures, Tmax, reached with an improved statistical accuracy, the mean and standard deviation of Tmax are quoted above for ten ignitions. However, to demonstrate the stochastic nature of the combustion process, the temperature temporal profiles in Figure 3 - 6 are presented for single ignitions only rather than as smeared-out averages over several ignitions. Thus, some of the variations in the shapes of the profiles apparent after about 15 ms are a consequence of the stochastic behavior of the flames within the field of view of the IR camera. The temperature temporal profiles produced by igniting a JP-10 droplet containing 200 nm diameter Al particles without (c) or with (d) the surfactant are presented in Figure 6. As for the Ti-Al-B particles, the surfactant reduced the ignition delay time from 1.5 ms to less than 0.5 ms and possibly increased the maximum flame temperature Tm (Al NPs - surfactant) = 2870 ± 280 K versus Tm (Al NPs) = 2710 ± 180 K. The reduction in Δt is less for the Al NPs than for the Ti-Al-B RMNPs, since the Al NPs were already well-dispersed throughout the JP-10 before adding the surfactant. After reaching the maximum temperature Tmax, the temperatures decreased as the fuel was consumed.

**4.3. Optical Ignition Videos**

A visualization of the combustion process is displayed in Figure 7 for two JP-10 Ti-Al-B RMNPs - surfactant droplets. Once the CO2 laser strikes the liquid droplet (t = 0 ms), part of the droplet vaporizes; this phase of evaporation is evident from the vapor cloud. During this phase, some of the nanoparticles also ignited as shown through the orange-colored sparks ejected from the droplets while the vapor expanded. At this stage, the JP-10 has not ignited yet. However, the burning nanoparticles ignited the JP-10 vapor as well leading to the oxidation of the JP-10 fumes. This process is also visualized in the Movies M1 and M2 (Supporting Information).

**4.4 UV-Vis Emission Spectroscopy**

      The UV-Vis emission spectra produced during ignition of a JP-10 droplet containing Ti-Al-B RMNPs without or with the surfactant are shown in Figures 8 and 9, respectively. The features in the UV-Vis emission spectra allow the atoms, molecules, and radicals formed by the oxidation of the JP-10 and the Ti-Al-B RMNPs to be identified in addition to the impurities introduced in the manufacture of the particles.

Initially, we will discuss the spectrum collected without the surfactant (Figure 8). First, the main group I alkali metal impurities lithium (Li), sodium (Na), and potassium (K) were detected (Table 2),[118](#_ENREF_118) which produced the largest peaks in the spec­trum by far. Li originated from the lithium aluminum hydride (LiAlH4) used to prepare the Ti-Al-B RMNPs. Second, emissions were detected from radicals known to dominate the UV-Vis spectra of hydrocarbon flames. The hydroxyl radical (OH) was assigned via four A2Σ+ - X2Π transitions which are distinguished by the different vibrational quantum numbers of the lower state, ν′, and upper state, ν. Dicarbon (C2) was identified by observing seven transitions of the Swan system, d3Πg – a3Πu.[39-40](#_ENREF_39), [119-120](#_ENREF_119) The formyl radical (HCO) could only be assigned tentatively via a single emission line at 358.8 nm (Table 2).[119](#_ENREF_119) Third, the data suggest that metal atoms evaporated from the Ti-Al-B RMNPs. Atomic aluminum could be detected through four transitions at 309.3 nm, 394.4-396.2 nm, 669.6-669.9 nm, and 783.5-783.6 nm, whereas titanium was identified via four emission lines at 363.5-365.3 nm, 375 nm, 394.9-395.8 nm, and 398.2-399.9 nm. In contrast, boron atoms were not detected. Considering the trend in the boiling points of pure aluminum, titanium, and boron of 2,743 K, 3,560 K, and 4,893 K, respectively, our spectra suggest that the flame temperature was sufficient to evaporate aluminum and titanium from the RMNP but not boron. The maximum flame temperature Tmax of 2550 ± 280 K (section 4.2) is consistent with the absence of emissions from gas-phase boron. Tmax is also below the boiling points of aluminum and titanium, though, which appears to contradict the observation of emissions from gas-phase Al and Ti atoms. However, the ignition temperature of Al particles is known to decrease with diameter; for example, from 2350 K for a diameter of 100 μm to 933 K for a diameter of 100 nm. A similar trend is expected for Ti. The aforementioned trends in the boiling points provide a qualitative rationale for the detection of gas-phase aluminum and titanium, but the absence of boron. Fourth, the emission spectra reveal the presence of rovibrationally excited metal monoxides, namely, aluminum monoxide (AlO), boron monoxide (BO), and titanium monoxide (TiO) via five, nine, and five emissions, respectively. The emissions of aluminum monoxide, which were also detected in the oxidation of JP-10 droplets doped with Al NPs,[65-68](#_ENREF_65) originate from the Δν = 2, 1, and 0 transitions of AlO (A 2Σ+ - X 2Σ+), where Δν denotes the change in the vibrational quantum number ν.[119](#_ENREF_119) Titanium monoxide produces a series of broad emissions, the largest of which have maxima at around 595, 623, 675, 713, and 777 nm. The lower two emissions are produced by B 3Π0,1,2 - X 3Δ1,2,3 transitions, whereas the highest three emissions are due to A 3Φ2,3,4 - X 3Δ1,2,3 transitions. The emissions near 595, 675, and 772 nm are partially hidden by the relatively much larger Na, Li, and K emission lines, respectively, although the 623 nm and 713 nm emissions appear as separate, broad bands with relatively small amplitudes.[121-124](#_ENREF_121) Rovibrati­o­nal­ly excited boron monox­ide can be distinguished by several emissions from the BO α-system, A2Π - X2Σ+ system. Finally, the boron dioxide (BO2) fluctuation bands are produced by A2Πu - X2Πg transitions and consist of waves showing maxima at 418, 453, 471, 490, 498, 519, 549, 581, 598, 610, and 640 nm. The BO2 emissions are significantly larger than the BO bands and consequently partly mask them. The rapid oxidation of boron monoxide to boron dioxide has been established in molecular beam studies.[125](#_ENREF_125) Similarly, the AlO emissions centred at 453, 471, and 490 nm overlap closely with the relatively much larger boron dioxide fluctuation emissions and, hence, do not appear as separate, distinct features. No higher oxides of aluminum, titanium, or boron were observed.

The UV-Vis emission spectrum produced during ignition of a JP-10 droplet containing Ti-Al-B nanoparticles coated with the surfactant is shown in Figure 9a. The spectra with and without the surfactant differ in several respects. First, since the ignition occurred when less of the JP-10 had evaporated, the emission features appeared superimposed on a grey-body background. Fitting a grey-body spectrum enabled the flame temperature to be determined and gave 2600 ± 40 K, which is consistent with the mean value of 2710 ± 180 K obtained from the IR camera (section 4.2). In Figures 9b and 9c, the same data are displayed except the grey-body background has been subtracted to illustrate the emission structure more clearly. In some spectral regions of the fits, broad underlying peaks were included to account for variations in the background or unresolved bands, but these are not assigned in Figure 9 or included in Table 2. The increased statistical inaccuracy introduced by the grey-body background obscured peaks e) - j), m), n), and p) produced by BO, BO2,K, Ti, and HCO which, in contrast, are clearly evident in Figure 8 without the surfactant. However, possibly because of the larger volume of combusting hydrocarbons available, an emission line appeared at 430 nm produced by the A 2∆ - X 2Π transition of the methylidyne radical (CH). The relative intensities of emissions from the alkali metals also differed with the surfactant; for example, the K line at around 770 nm is smaller whereas the Na line at 770 nm is larger. Broad bands between approximately 800 nm and 1000 nm appeared with the surfactant, which are due to emissions or absorptions from highly-excited vibrational states of water molecules. The broad absorption region from approximately 900 nm to 1000 nm could be because of the water vapor produced in the combustion or absorption by the optical fiber.

**4.5 FTIR Spectroscopy**

      Similar to the FTIR transmission spectra obtained for the oxidation of Al NP doped JP-10,[65-68](#_ENREF_65) the FTIR data collected after the combustion of the droplet revealed the gaseous products of the oxidation to be solely carbon dioxide (CO2) and water (H2O). These cover the asymmetric stretching mode (νas(H2O)) (3756 cm-1) along with the bending mode (δ(OH)) (1600 cm-1) of water. Carbon dioxide was identified via two combination bands (1(σg+) +3(σu+),1(σg+) +3(σu+)) at 3714 and 3612 cm-1, respectively. Further absorptions were detected for the asymmetric stretching (σu+) (2347, 2359, 2279 cm-1) and bending modes (πu) (668, 648, 619, 655, 680, 720 cm-1) modes.

**4.6      Computational Results**

**4.6.1.  Gas Phase Reaction of Atoms with JP-10**

The detection of aluminum (Al, 2P) and titanium atoms (Ti, 3F) in the emission spectra necessitates an investigation of their reactivity with JP-10 molecules in the gas phase (Table S2). Although atomic boron was not observed, the calculations were expanded to the boron (B, 2P) – JP-10 system for completeness. The reactions of Al(2P), B(2P), and Ti(3F) with JP-10 lead via hydrogen abstraction to six chemically distinct JP-10 radicals (R1-R6) (Figure 2) in overall endo­ergic reactions of 77-120, 129 –173, and 217–262 kJ mol-1 for the alumi­num, boron, and titanium systems, respectively. This correlates with the weaker metal – hydrogen single bond compared to the cleaved carbon-hydrogen bond. Overall, the strong endoergic nature of these reactions make these reactions unfavorable.

**4.6.2.  Gas Phase Reaction of Oxides with JP-10**

The detection of aluminum monoxide (AlO), boron monoxide (BO), and titanium monoxide (TiO) in the emission spectra motivated a computational exploration the reactivity of these mono oxides with JP-10 molecules in the gas phase. Since the overall hydrogen abstractions by titanium monoxide (TiO) are highly endoergic by 209 (R1 + TiOH), 248 (R2 + TiOH), 231 (R3 + TiOH), 214 (R4 + TiOH), 204 (R5 + TiOH), and 205 kJ mol-1 (R6 + TiOH), these reactions are not competitive with the hydrogen abstractions by aluminum monoxide (AlO) and boron monoxide (BO) as detailed below. Consequently, complete potential energy surfaces are only computed for the abstraction of hydrogen from JP-10 by aluminum monoxide (AlO) and boron monoxide (BO) (Table S3; Figures 10-12). In each system, the metal mono oxide and JP-10 yield van-der-Waals complexes in the entrance channel (vdW I). Formation of these van-der-Waals complexes is governed by attractive, long range dipole (metal monoxide) – dipole (JP-10) interactions. Once again, since JP-10 holds six non-equivalent hydrogen atoms, six chemically non-equivalent van-der-Waals complexes exist in the entrance channel.

Considering the AlO-JP-10 system (Figures 10-12, Table S3), the van-der-Waals complexes at sites 3-6 are weakly stabilized by 8 to 48 kJ mol-1 with with respect to the separated reactants. At all 6 sites, the reactants were found to isomerize via hydrogen abstraction to a van-der-Waals complex of aluminum monohydroxide (AlOH) plus the JP-10 radical (VdW II). It is important to note that the hydrogen abstraction processes involve an abstraction of the hydrogen with the oxygen atom of the aluminum monoxide radical; further, the transition states are located above the energy of the separated reactants by 4 to 20 kJ mol-1. The resulting VdW II complexes reside in potential energy wells of 71 to 109 kJ mol-1 with respect to the separated reactants and may undergo unimolecular decomposition to the JP-10 radicals (R1 – R6) and aluminum monohydroxide (AlOH) in overall exoergic reactions releasing 4 to 45 kJmol-1.

With respect to the BO-JP-10 system (Figures 10-12, Table S3), the van-der-Waals complexes are stabilized by 6 to 10 kJ mol-1 with respect to the separated reactants and isomerize via hydrogen abstraction to a van-der-Waals complex of boron hydride oxide (HBO) plus the JP-10 radical (VdW II). Considering the stronger H-B versus Al-H bond, it is important to rationalize that the boron monoxide (BO) radical abstracts the hydrogen from JP-10 with the boron atom, but the aluminum monoxide abstracts atomic hydrogen with the oxygen atom. The transition states are located above the energy of the separated reactants by 1 to 28 kJ mol-1. The VdW II complexes are stabilized by 11 to 54 kJmol-1 with respect to the separated reactants and fragment via unimolecular decomposition to the JP-10 radicals (R1 – R6) and boron hydride oxide (HBO) in overall exoergic reactions (-31 to – 74 kJ mol-1).

**4.6.3.  Gas Phase Reaction of Dioxides with JP-10**

Boron dioxide (BO2, X2Σg+) represents the only dioxide detected via UV-Vis spectroscopy; neither aluminum dioxide (AlO2, X2Σg+) nor titanium dioxide (TiO2, X1A1) was observable in emission. The abstraction pathways of boron dioxide (BO2) do not involve the formation of initial van-der-Waals complexes, but proceed directly from the reactants via six distinct transition states located between 5 and 29 kJ mol-1 above the separated reactants (Figures 13-14, Table S4). These transition states connect the reactants with a van-der-Waals complex in the exit channel of meta boric acid (HOBO) and six distinct JP-10 radicals (R1 – R6). These complexes are stabilized by 56 to 90 kJ mol-1 with respect to the separated reactants and undergo unimolecular decomposition to the JP-10 radicals (R1 – R6) and meta boric acid (HOBO) in overall exoergic reactions (-35 to – 60 kJ mol-1).

**4.6.4. Gas Phase Reaction of O(3P) with JP-10**

As an atomic oxidizer, the potential energy surfaces of ground state oxygen atoms with JP-10 are more diverse compared to the aluminum monoxide and boron monoxide – JP-10 surfaces as detailed in Figures 15-16 and Tables S5 and S7. Essentially, O(3P) can abstract atomic hydrogen from one of the six chemically non-equivalent C-H bonds of JP-10. However, these abstraction routes are not initiated by the formation of van-der-Waals complexes between atomic oxygen and JP-10 in the entrance channel, but proceed from the reactants via six distinct transition states located 28 to 43 kJ mol-1 above the separated reactants. Prior to the formation of the separated products, all pathways involve van-der-Waals complexes in the exit channels of which four are below (-12 - -17 kJ mol-1; R1, R4-R6), but two are above (+8 - + 20 kJ mol-1; R2, R3) the energies of the separated products. Correspondingly, our calculations suggest that three exit channels to R1, R5, and R6 plus the hydroxyl radical are weakly exorgic by -2, -6, and -4 kJmol-1, respectively, whereas three exit channels to R2, R3, and R4 plus hydroxyl are endoergic by 34 19, and 3 kJ mol-1, respectively. However, it shall be stressed that the formation of each of the R1-R6 radicals along with the hydroxyl radical has to pass a transition state, which is located above the energy of the separated reactants (Figures 10-12).

It shall be highlighted that in the O(3P) – JP-10 system, the lowest energy transition state is located 28 kJ mol-1 above the separated reactants; in this pathway, atomic hydrogen is abstracted from the C4 position leading effectively to a van-der-Waals complex between the hydroxyl radical and R4. For the BO, AlO, and BO2 abstraction pathways – with the exception of the transition state connecting the reactants to the van-der-Waals complex between metaboric acid (HOBO) and the R6 radical, all transition states are *lower* than 29 kJmol-1. Consequently, BO, AlO, and BO2 are expected to abstract atomic hydrogen faster from the JP-10 reactant than O(3P).

**4.6.5. Gas Phase Reaction of O2(X3Σ−g) with JP-10**

Considering the weaker H-O bond in the hydroxyperoxy radical (HO2, X2A’) compared to the C-H bond strengths in JP-10, the hydrogen abstraction pathways of molecular oxygen from JP-10 are overall highly endoergic between 202 and 242 kJmol-1 (Figures 17-18, Table S5). Similar to atomic oxygen, no van-der-Waals complexes could be located in the entrance channel, and the abstraction reaction may pass six distinct transition states located between 188 and 209 kJ mol-1 above the separated reactants. Prior to the formation of the separated reactants, the JP-10 radicals R1 – R6 form six distinct van-der-Waals complexes with the hydroxyperoxy radical. These are located between 183 to 208 kJmol-1 above the energies of the separated reactants before they compose in overall endoergic reactions (202 - 242 kJ mol-1) to the JP-10 radicals (R1-R6) along with the hydroxyperoxy radical (HO2, X2A’).

**5. Conclusions**

           This work represents the first report on the combustion of single levitated droplets of JP-10 doped with Ti-Al-B-based RMNPs in an oxygen (60 %) – argon (40 %) atmosphere utilizing an ultrasonic levitator. Droplets were ignited by a carbon dioxide laser and the oxidation processes were observed by following FTIR and UV-Vis spectroscopies along with infrared thermal imaging and high-speed optical cameras. This study resulted in interesting findings.

*First*, recall that under the same experimental conditions, pure JP-10 droplets did not ignite.[65-68](#_ENREF_65) Monitored via the high-speed optical camera, the carbon dioxide laser led to the evaporation of the droplet prior to the autoignition temperature of JP-10 of 509 K. The addition of RMNPs could have increased the boiling point of JP-10. However, JP-10 droplets doped with silicon dioxide (SiO2), titanium dioxide (TiO2), aluminum oxide (Al2O3), and copper (II) oxide (CuO) nanoparticles of comparable size to the Ti-Al-B RMNPs did not ignite either.[65-66](#_ENREF_65), [68](#_ENREF_68) Consequently, the RMNPs must have played an active role in the ignition of the JP-10.

*Second*, the UV-Vis emission spectra revealed the presence of gas phase aluminum (Al) and titanium (Ti) atoms. Recalling the trends of boiling points of aluminum (2,743 K), titanium (3,560 K), and boron (4,893 K), typical flame temperatures of 2550 ± 280 K, which are higher than the boiling point of aluminum and should lead to a sufficient vapor pressure of Titanium to be detected spectroscopically, are sufficient to evaporate aluminum and titanium, but not boron. These atoms can be oxidized in the gas phase by molecular oxygen to UV-Vis spectroscopically detected aluminum monoxide (AlO) and titanium monoxide (TiO) intermediates in overall exoergic reactions of 14 and 170 kJ mol-1, respectively.[126](#_ENREF_126) These detected transient species rationalize the X-ray powder diffraction identification of the terminal end products of oxidation of titanium dioxide (TiO2) and aluminum oxide (Al2O3) in solid residues of RMNPs doped n-decane flames.[57](#_ENREF_57) The analysis of the optical ignition videos also supports that the nanoparticles are ignited prior to the oxidation of JP-10 as evident from the orange-colored sparks emitted from the droplets while the vapor expanded. Considering the absence of gas phase boron atoms, the detection of boron monoxide (BO) proposed active surface chemistry through oxidation of the RMNPs and the release of at least boron monoxide (BO) into the gas phase. The oxidation of gas phase boron monoxide (BO) by molecular oxygen to boron dioxide (BO2) plus atomic oxygen is exoergic by 76 kJ mol-1 and hence could operate in the gas phase, although an involvement of surface oxidation processes of RMNPs to form boron dioxide (BO2) cannot be discounted. Note that emission lines from boron dioxide (BO2) were also observed in n-decane[57](#_ENREF_57) as well as methane flames doped with RMNPs.[59](#_ENREF_59) The elevated temperature of methane flames also resulted on emissions from aluminum monoxide (AlO). Finally, the UV-Vis emission spectra revealed key reactive intermediates (OH, CH, C2, HCO) of the oxidation of JP-10.

*Third*, electronic structure calculations reveal that reactive radicals have a profound impact on the oxidation of JP-10. Although titanium monoxide (TiO) can react to produce titanium dioxide (TiO2) powders,[57](#_ENREF_57) TiO does not engage in an active JP-10 chemistry as all of its abstraction pathways are highly endoergic by at least 209 kJ mol-1. This is similar to atomic alu­minum and boron, whose hydrogen abstraction reactions from JP-10 are endoergic by at least 77 and 129, respectively. Therefore, aluminum and titanium react pre­ferentially with molecular oxygen to form their monoxides as detected spectroscopically. The formation of gas-phase boron monoxide (BO), aluminum monoxide (AlO), and boron dioxide (BO2) supplies a highly reactive pool of radicals, which can abstract hydrogen from JP-10 via low lying transition states ranging only 1 (BO), 4 (AlO), and 5 kJ mol-1 (BO2) above the separa­ted reactants thereby forming JP-10 radicals R1-R6 (Figure 2) along with the hydrogen abstraction products HBO, AlOH, and HOBO in overall exoergic reactions. The hydrogen atoms are abstracted preferentially from the bridging methylene moiety (CH2) or methylidyne functional group (CH) leading to R3 and R4, respectively. Importantly, these abstraction barriers are well below the barriers of abstractions for ground-state atomic oxygen and molecular oxygen which exceed 28 and 188 kJmol-1, respectively. In this sense, gas-phase boron monoxide, aluminum monoxide , and boron dioxide catalyze the oxidation of gas-phase JP-10 via hydrogen abstraction thereby forming highly reactive JP-10 radicals such as R3 and R4, which can then react barrierlessly via rapid radical – atom/molecule reaction involving atomic and molecular oxygen and hence drive the oxidation of JP-10. Therefore, the addition of RMNPs to JP-10 not only provides a higher energy density fuel but is expected to lead to shorter ignition delays compared to pure JP-10 owing to the highly reactive pool of BO, AlO, and BO2 radicals formed in the initial stages of the oxidation process. These predicted reduced ignition delays were observed by Epshteyn et al. in RMNPs doped JP-5.[61](#_ENREF_61) Overall, the studies presented here represent the first step toward a systematic understanding of the oxidation of JP-10 doped with RMNPs.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information given below is available free of charge on the ACS publications website.

1. Calibration curves used to calibrate the (a) low energy region of Raman data (100 cm-1-2400 cm-1) and (b) high energy region of Raman data (2200 cm-1- 4000 cm-1) (PDF).
2. Comparison between the calculated vibrational wavenumber and (a) the experimental Raman wavenumber and (b) the experimental FTIR wavenumber of the normal modes of e*xo*-tetrahydrodicyclopentadiene (PDF).
3. Raman spectra of (a) pure JP-10, (b) JP-10-Al, and (c) JP-10-Ti-Al-B NPs (RMNPs) (PDF).
4. FTIR spectra of pure JP-10 (PDF).
5. Raman spectra of new peaks resulting from photochemically activated JP-10-Ti-Al-B NPs (RMNPs) by a tightly focused 532 nm laser beam (45 – 50 µm) at 1 kHz (PDF).
6. Vibrational Mode Assignments for the Observed Peaks in the Raman Spectra of JP-10, JP-10-Al, and JP-10-Ti-Al-B NPs (RMNPs), Ti-Al-B NPs (RMNPs), and the FTIR Spectra of JP-10 (PDF).
7. Total energies and zero point energy corrected total energies simulated for the transition states, reactive intermediates, complexes, and the products for the reactions between AlO, BO, BO2 with JP-10 (PDF).
8. Cartesian coordinates and vibrational frequencies of van-der-Waals complexes, transition states and products of the reactions of BO, AlO, and BO2 with JP-10 (PDF).
9. cartesian coordinates and vibrational frequencies of van-der-Waals complexes (vdW), transition states (TS), and products of the reactions of atomic and molecular oxygen with JP-10 (PDF).

(10) Optical high-speed videos (M1 and M2) of the ignition of JP-10 droplet containing RMNPs and surfactant (PPT).

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