Supporting Information

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

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1. Absorption background from nitrogen dioxide in the Raman spectrum of a levitated droplet



Figure S1. Raman spectra of a levitated JP-10 droplet containing Al nanoparticles after laser irradiation and interaction with NO₂ (black circles) in the (a) 4000 - 2400 cm⁻¹ and (b) 2400 - 150 cm⁻¹ Raman-shift ranges compared with the NO₂ absorption spectrum measured by Bogumil et al (blue circles).¹ The total fit to the spectra (red lines) and the individual peak fits (green lines) are included for the levitated sample. A background has been subtracted from the spectra of the processed sample.

Table S1. Wavenumbers and vibrational modes assignments for the peaks observed in the Raman spectrum of JP-10.

Peak	Wavenumber	Reference	Number ^{a)}	Vibrational
	(cm ⁻¹)	wavenumber ^{a)}		mode ^{a)}
	without Al	(cm ⁻¹)		
а	2949 ± 1	2955	68	CH stretch
b	2905 ± 1	2912	62	CH ₂ stretch
с	2862 ± 1	2868	57	CH stretch
d	1479 ± 1	1472 ± 6	55	CH ₂ scissor
e	1453 ± 1	1454	54	CH ₂ scissor
f	1334 ± 2	1337	47	CH wag
g	1311 ± 11	1315 ± 3	44	CH ₂ wag
h	1294 ± 4	1300 ± 8	41	CH wag
i	1278 ± 2	1284	40	CH ₂ wag
j	1225 ± 1	1228	37	CH ₂ rock
k	1198 ± 1	1202	35	CH ₂ twist
1	1167 ± 3	1169	33	CH ₂ twist
m	1141 ± 1	1145	32	CH ₂ twist
n	1127 ± 1	1130	31	CH ₂ twist
0	1111 ± 1	1115	30	Rock, CH ₂ twist
р	1054 ± 1	1057	29	CH ₂ Wag
q	1031 ± 1	1035	26	CH ₂ Twist
r	982 ± 1	988	24	CC stretch
s	945 ± 1	948	22	Ring breathing
t	913 ± 1	919	20	CH ₂ twist
u	879 ± 1	884	17	CC stretch
v	849 ± 2	857	15	CCC bend
w	812 ± 1	817	14	CH ₂ rock
х	782 ± 1	785	13	CC stretch
у	741 ± 1	746	12	CC stretch
z	656 ± 12	-	-	-
a	611 ± 7	-	-	-
b	546 ± 1	552	9	CCC bend
c	523 ± 2	527 ± 3	8	Ring twist
d	484 ± 1	490	7	CCC bend
e	398 ± 3	396	6	CCC bend
f	320 ± 6	-	-	-
g	263 ± 2	-	-	-

^{a)}Ref. [2]

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.



Figure S2. FTIR absorption spectrum before igniting a JP-10 droplet containing aluminum nanoparticles when levitated in 60% O₂, 39% Ar, and 1% NO₂. The rovibrational bands labelled (a) - (e) are assigned in Table S2. The total fit (red line) and individual peak fits peaks (green lines) are shown.



Figure S3. FTIR absorption spectrum after igniting a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O₂, 39% Ar, and 1% NO₂.



Figure S4. Difference, Δ (absorbance), between the absorbance spectra after (Figure S3) and before (Figure S2) igniting a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O₂, 39% Ar, and 1% NO₂. The newly formed rovibrational bands are labelled (a) - (h) and assigned in Table S3. The total fit (red line) and the individual peak fits peaks (green lines) are shown. The dips labelled with the asterisks are produced by small reductions in the concentrations of NO₂ and N₂O₄.

Table S2. Vibrational mode assignments for bands (a) - (e) in the FTIR absorption spectrum (Figure S2) before igniting a JP-10 droplet containing aluminum nanoparticles when levitated in 60% O₂, 39% Ar, and 1% NO₂.

Band	Centre	Molecule	Ref.	Number ^{b)}	Symmetry ^{b)}	Vibrational
	wavenumber		band center			mode ^{b)}
	$(cm^{-1})^{a)}$		(cm^{-1})			
a	2906	NO ₂		1 + 3	a ₁ + b ₁	Combination
						mode
b	1751	N ₂ O ₄	1749.2 ^{b)}	9	b _{2u}	
c	1616	NO ₂	1617.8 ^{b)}	3	b ₁	antisymm.
						stretch
d	1261	N ₂ O ₄	1261.08 ^{b)}	11	b _{3u}	
e	750	NO ₂	749.65 ^{b)}	2	a ₁	Bend

^{a)}Uncertainties are less than 1 cm⁻¹. ^{b)}Ref. [3] Table S3. Vibrational mode assignments for bands (a) - (h) in Figure S4, which shows the difference between the FTIR absorbance spectra after (Figure S3) and before (Figure S2) igniting a JP-10 droplet containing aluminum nanoparticles initially levitated in 60% O₂, 39% Ar, and 1% NO₂.

Band	Centre	Molecule	Ref.	Number	Symmetry	Vibrational
	wavenumber ^{a)}		band center			mode ^{b)}
	(cm^{-1})		(cm^{-1})			
а	3714	CO ₂	3714.8 ^{c)}	1 + 3	$\sigma_g^{+} + \sigma_u^{+}$	combination band
b	3612	CO ₂	3612.8 ^{c)}	1 + 3	$\sigma_g^{+} + \sigma_u^{+}$	combination band
c	2959	C10H16	2942 ^d)	68		v(CH)
d	2932 ± 5	C10H16	2913 ^{d)}	62		v(CH ₂)
e	2879	C10H16	2865 ^{d)}	57		v(CH)
f	2349	CO ₂	2349.1 ^{c)}	3	σ_{u}^+	$v_{as}(CO_2)$
g	≈1600	H ₂ O	1595 ^{e)}	2	a 1	δ(OH)
h	668	CO ₂	667.4 ^{c)}	2	$\pi_{ m u}$	$\delta(CO_2)$

^{a)}Uncertainties are less than 1 cm⁻¹ unless stated otherwise.

^{b)}v denotes stretch; δ , bend; and as, antisymmetric.

^{c)}Ref. [4],^{d)}Ref. [2],^{e)}Ref. [3].

3. Does absorption from nitrogen dioxide reduce the apparent temperature measured by the infrared camera?

The absorbance A is defined by

$$A = \log_{10} \frac{I_0}{I} \tag{S1}$$

where I_0 is the radiant flux emitted by the source and I is the radiant flux reaching the detector. The absorbance of the infrared beam through the full width w of 37.6 cm inside the process chamber containing a 60% O₂, 35% Ar, and 5% NO₂ gas mixture is shown in Figure S5.



Figure S5. Absorbance of the infrared beam within the process chamber for a 60% O₂, 35% Ar, and 5% NO₂ Ar gas mixture.

The black-body radiation originates from the igniting droplet in the centre of the chamber, and so the path length of the radiation within the NO₂ gas mixture is w/2. The transmission of the black-body radiation within the chamber, I/I_0 , is therefore given by $10^{-A/2}$, where A is the absorbance shown in Figure S5 and here I denotes the radiant flux reaching the infrared camera. The infrared camera determines the temperature by measuring the total radiation power in the 3 µm to 5 µm wavelength range, which corresponds to a wavenumber range of 3333 cm⁻¹ to 2000 cm⁻¹. The effect of the absorption of the infrared radiation by the NO₂ on the black-body spectrum from 3 µm to 5 µm for a typical ignition temperature of 2500 K is presented in Figure S6. By integrating the area under the curve shown in Figure S6 with or without absorption by the NO₂, we determined that the nitrogen dioxide reduces the power reaching the infrared camera by the factor of 0.932. According to the Stefan-Boltzmann law, the power radiated by a black-body varies in proportion to the fourth power of the temperature T, that is,

 $P \propto \sigma T^4$

(S2)

where σ is the Stefan-Boltzmann constant. Therefore, the reduction in the power of 0.932 will cause the apparent temperature to reduce by the factor of 0.982. The required correction factor of 1.018, although small, has been applied to the temperature temporal profile with NO₂ shown in Figure 8. We note that the correction factor for an uncooled infrared radiation

detector operating in the 7 μm to 14 μm wavelength range would be significantly larger with the value of 1.053.



Figure S6. The effect of absorption by NO₂ on the black-body spectrum produced at a temperature of 2500 K in the 3 μ m to 5 μ m wavelength range.

References

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(2) Lucas, M.; Brotton, S. J.; Min, A.; Pantoya, M. L.; Kaiser, R. I., Oxidation of levitated exo-tetrahydrodicyclopentadiene droplets doped with aluminum nanoparticles. *J. Phys. Chem. Lett.* **2019**, *10*, 5756-5763.

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4. Infrared thermal imaging videos of igniting JP-10 droplets containing Al nanoparticles with or without nitrogen dioxide

Movie M1. Infrared thermal-imaging video 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.

Movie M2. Infrared thermal-imaging video of an igniting JP-10 droplet doped with a 1% concentration of 100 nm-diameter untreated Al particles initially levitated in 60% O₂, 35% Ar, and 5% NO₂.

The temperature range of the infrared camera was set to the highest interval of 1670 - 3040 K for Movies M1 and M2. To enable the ignition processes to be viewed, the videos have been slowed down by a factor of 100. After ignition, the burning droplet can be observed to fall - within the field of view of the infrared camera - to hit the bottom ultrasonic transducer plate after 47 ms and 42 ms without and with NO₂, respectively. The splash produced by the impact releases an increased surface area for combustion. Consequently, as can be seen in the infrared videos, after approximately 50 ms the temperature increases again as the flames rise into the centre of the field of view of the infrared camera. However, only the data well before the droplet hits the transducer plate is presented or discussed elsewhere in the paper.