Supporting Information

Untangling the Efficient Boron-Initialized Hydroxyl-Terminated Polybutadiene Combustion for High Energetic Solid Propulsion Systems

Grace L. Rizzo,[1] Souvick Biswas,[1] Dongwon Ka[2], Xiaolin Zheng,[*2] Ralf I. Kaiser[*1]

[1]Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, USA

[2]Department of Mechanical Engineering, Stanford University, Stanford, CA 94305-3032, USA

*E-mail: ralfk@hawaii.edu

*E-mail: xlzheng@stanford.edu

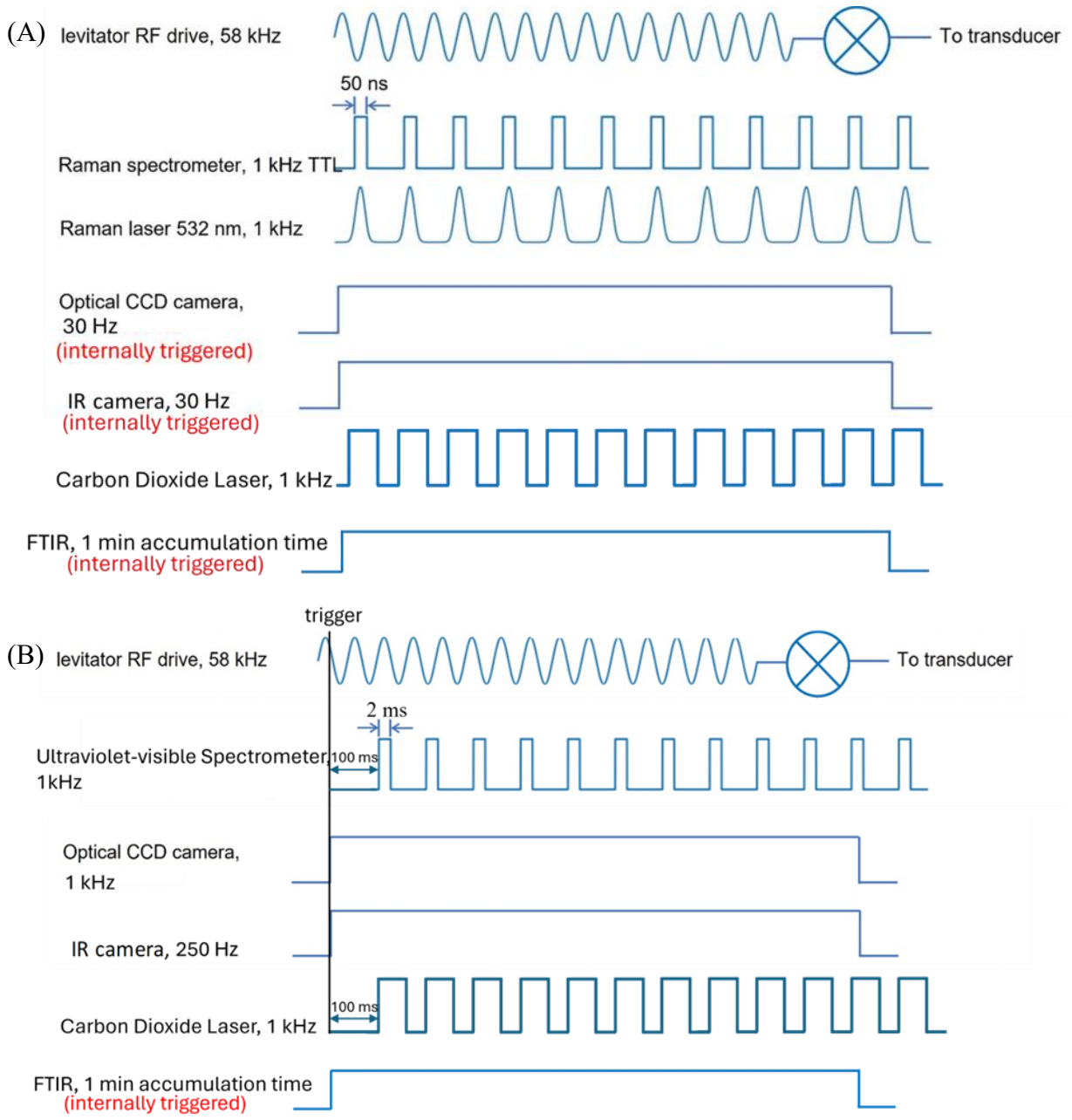

Figure S1. (A) Typical pulse sequence used for operation of the ultrasonic levitator for the heating of HTPB and B/HTPB in 100% Ar. Both Optical and IR camera were internally triggered and run at 30 Hz. (B) Typical pulse sequence used for operation of the ultrasonic levitator for the heating of HTPB and B/HTPB in 20% O_2 and 80% Ar.

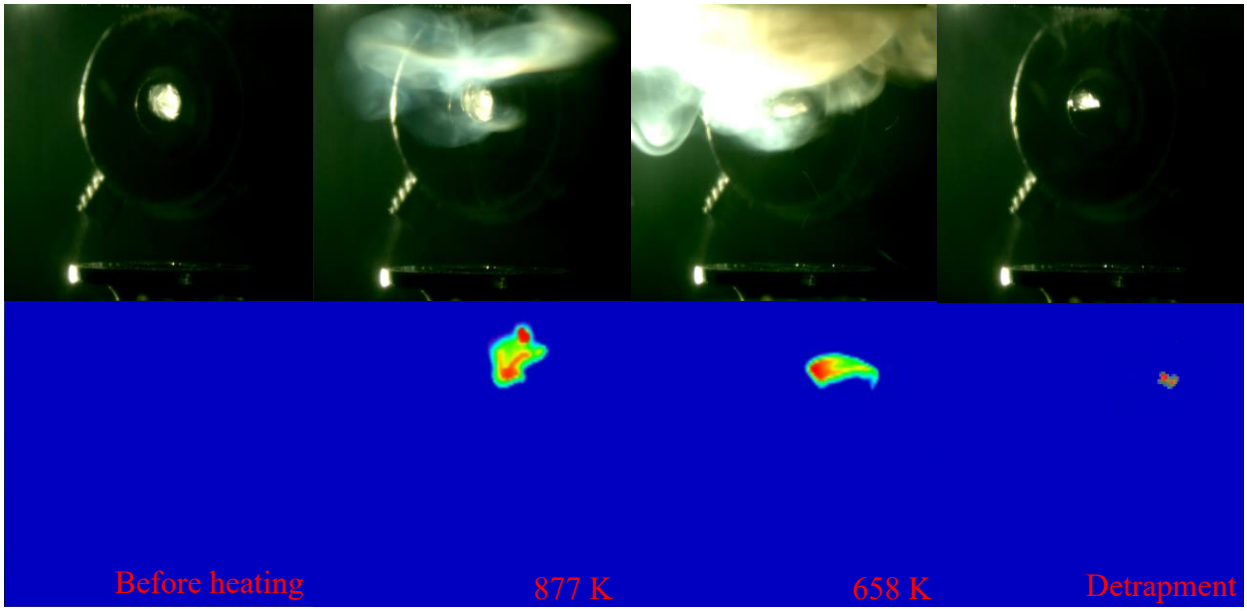

Figure S2. Optical and Infrared camera images of HTPB heated in 20% O_2 and 80% Ar.

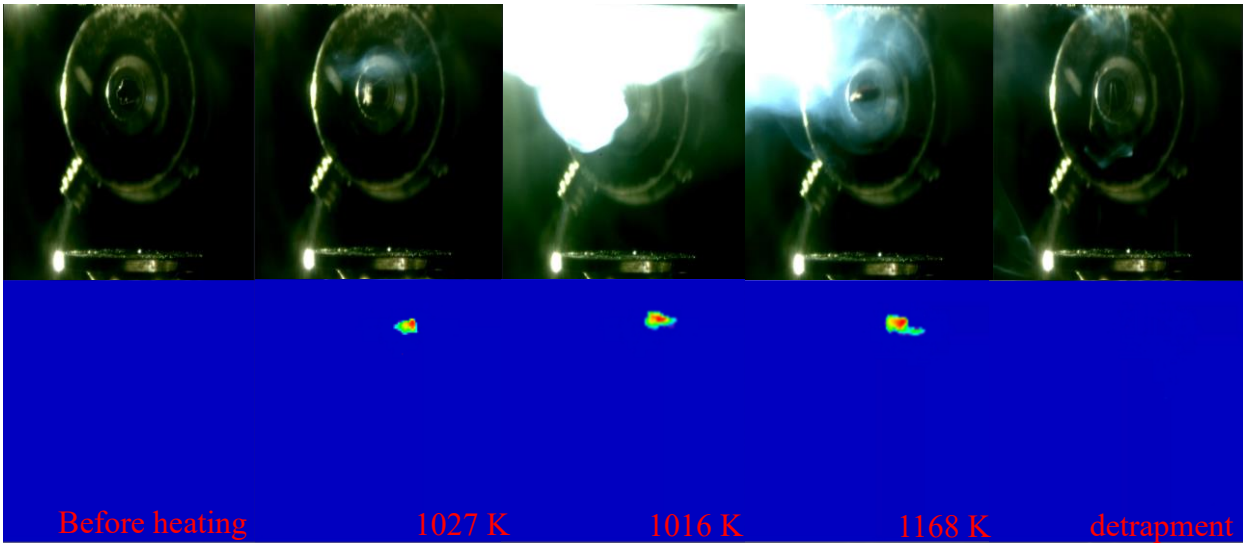

Figure S3. Optical and Infrared camera images of B/HTPB heated in 100% Ar.

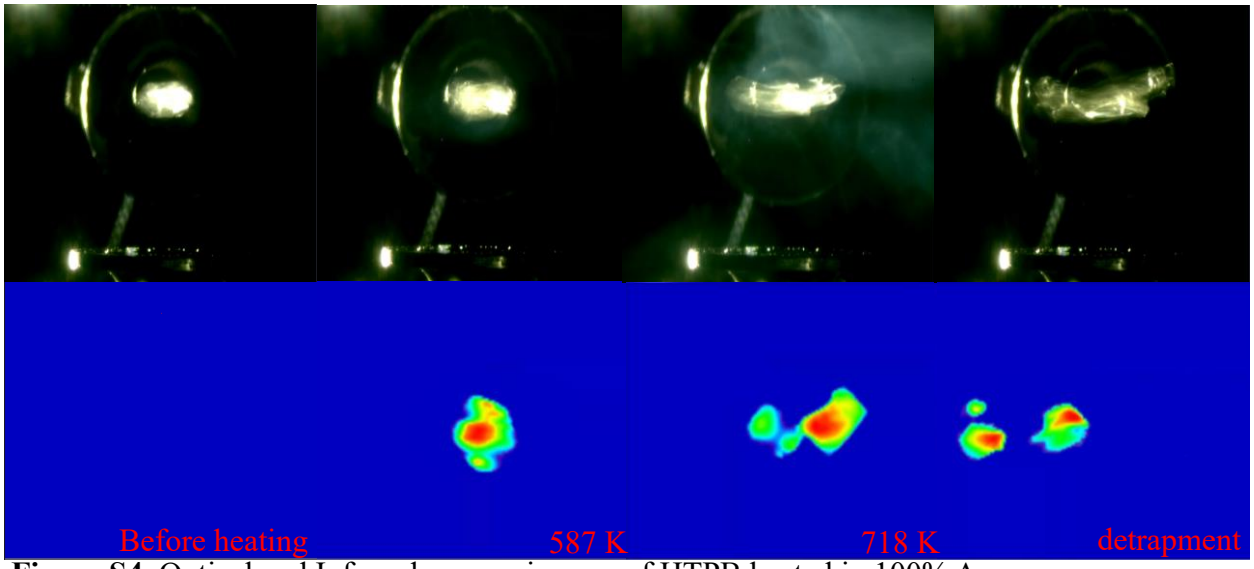

Figure S4. Optical and Infrared camera images of HTPB heated in 100% Ar.

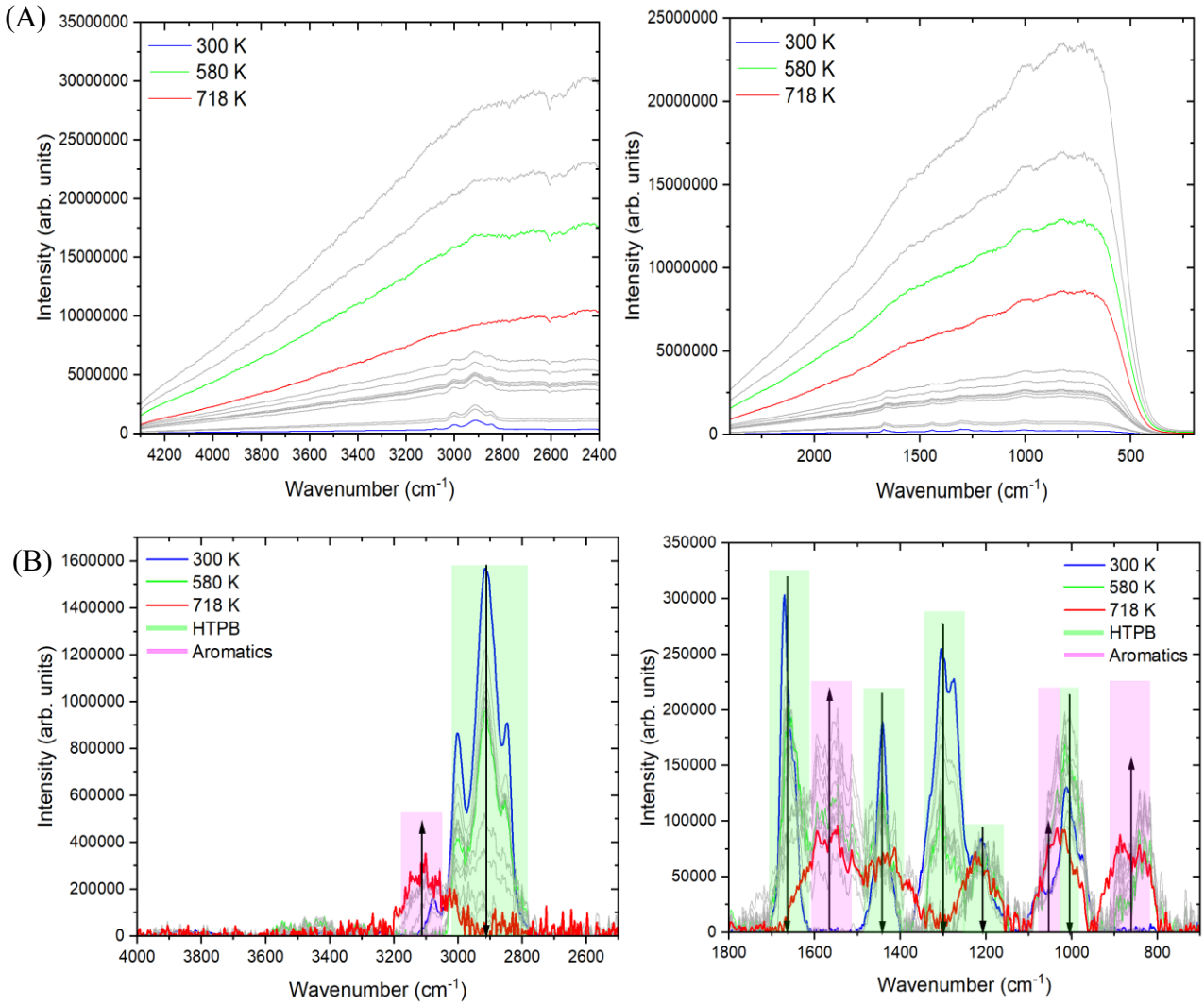

Figure S5. (A) Raman spectra of HTPB from 300 to 718 K in 100% Ar. Left panel represents the high wavenumber region and the right panel represents the low wavenumber region. (B) Baseline subtracted Raman spectra from (A).

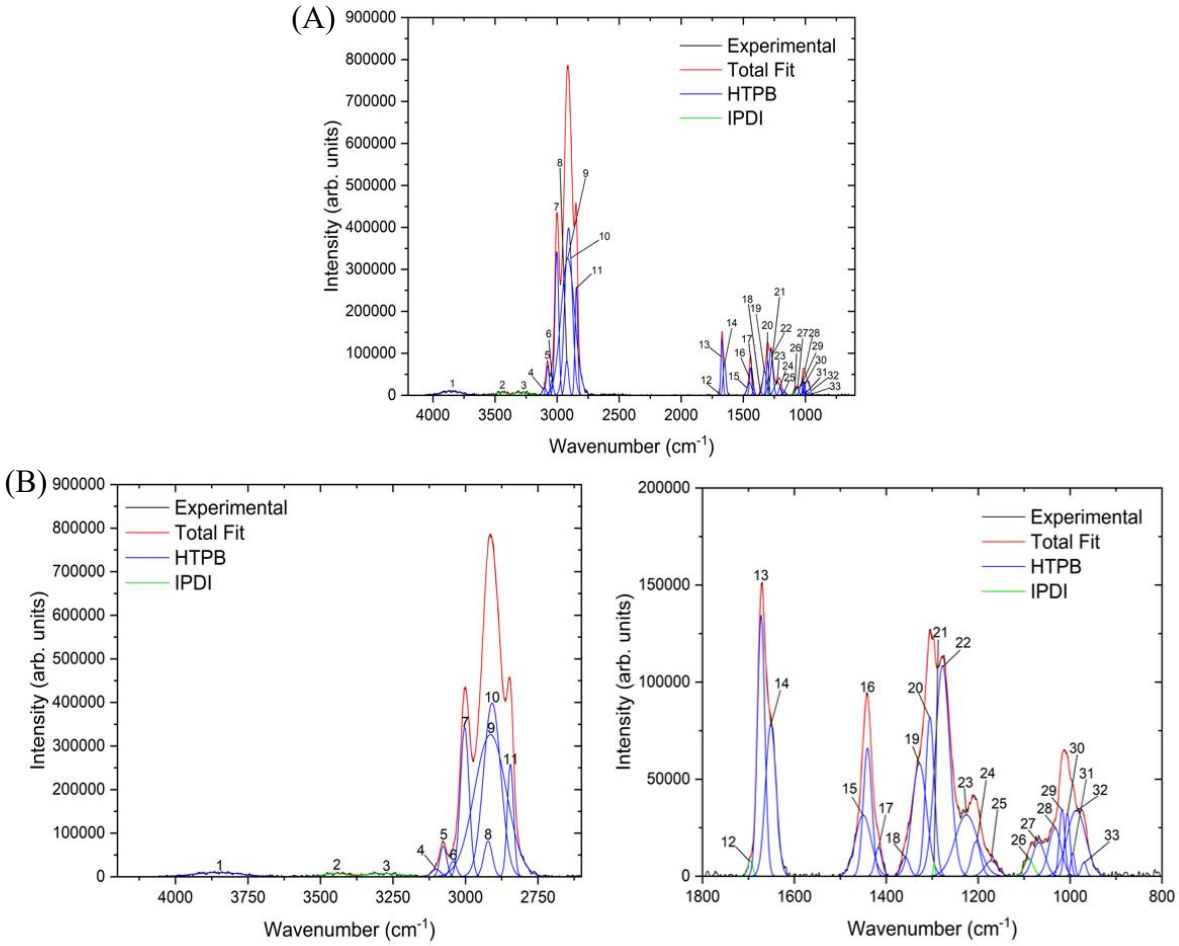

Figure S6. Room temperature deconvoluted Raman spectra of HTPB in 100% Ar. (A) represents the full spectrum and (B) represents the zoomed in high and low wavenumbers of the spectrum in (A).

Table S1. Peak assignments for the deconvoluted Raman spectrum of the HTPB particle levitated in 100% Ar at 300 K.

Peaks	Experimental Frequency (cm^{-1})	Literature Frequency (cm^{-1})[1,2,3]	Assignment	Carrier
1	3854	3800-3400	ν O-H	-CH_2-OH
2	3447	3340-3250	ν N-H	(associated) -NH-CO-O-
3	3283	3340-3250	ν N-H	(associated) -NH-CO-O-
4	3101	3095-3070	ν =C-H	-CH=CH_2
5	3076	3080 3095-3070	ν_a CH_2= ν =C-H	CH_2 -CH=CH_2
6	3042	3050	ν =C-H	alkene
7	3003	3011-3004	ν CH=CH	alkene
8	2922	2990-2900 2940-2915	ν_a CH_2 ν_a CH	-CH_2-OH -CH_2-
9	2914	2990-2900	ν_a CH_2	-CH_2-OH
10	2908	2909-2903	ν_a CH_2	CH_2
11	2845	2855-2845 2885-2865	ν_s CH_2 ν_s C-H	CH_2 CH_3
12	1696	1740-1680	ν C=O	alkyl urethane
13	1672	1671	ν_s C=C	alkene
14	1651	1656	ν_s C=C	alkene
15	1450	1480-1410 1451-1450	δ CH_2 δ_s CH_2	-CH_2-OH CH_2
16	1441	1465-1440 1443-1440	δ_a C-H δ_s CH_2	CH_3 CH_2
17	1417	1440-1260	δ O-H	-CH_2-OH
18	1359	1355 1440-1260 1390-1370	ω CH_2 δ O-H δ_s C-H	CH_2 -CH_2-OH -C-CH_3
19	1328	1324 1440-1260	ω CH_2 δ O-H	CH_2 -CH_2-OH
20	1305	1440-1260 1308	δ O-H δ =CH	-CH_2-OH alkene
21	1296	1265-1200	ν C-N ν C-O	Urethane
22	1278	1440-1260 1277	δ O-H τ CH_2	-CH_2-OH CH_2
23	1226	1295-1200	ρ_s CH	alkene
24	1205	1208-1201	τ CH_2	CH_2
25	1172	1150-1075	ν C-O	-CH_2-OH
26	1090	1090-1040	ν C-O	urethane
27	1068	1090-1000 1090-1040	ν CCO ν C-O	-CH_2-OH urethane

28	1033	1027 1030	ν C-C ring deformation	alkane cycloalkane
29	1017	1018 1090-1000	ν C-C ν CCO	alkane
30	1006	1011-1009 1055-1000	ν C-C C-C skeletal	alkane cycloalkane
31	994	995-969	ω CH	alkane alkene
32	986	995-969	ω CH	alkane alkene
33	970	995-969	ω CH	alkane alkene

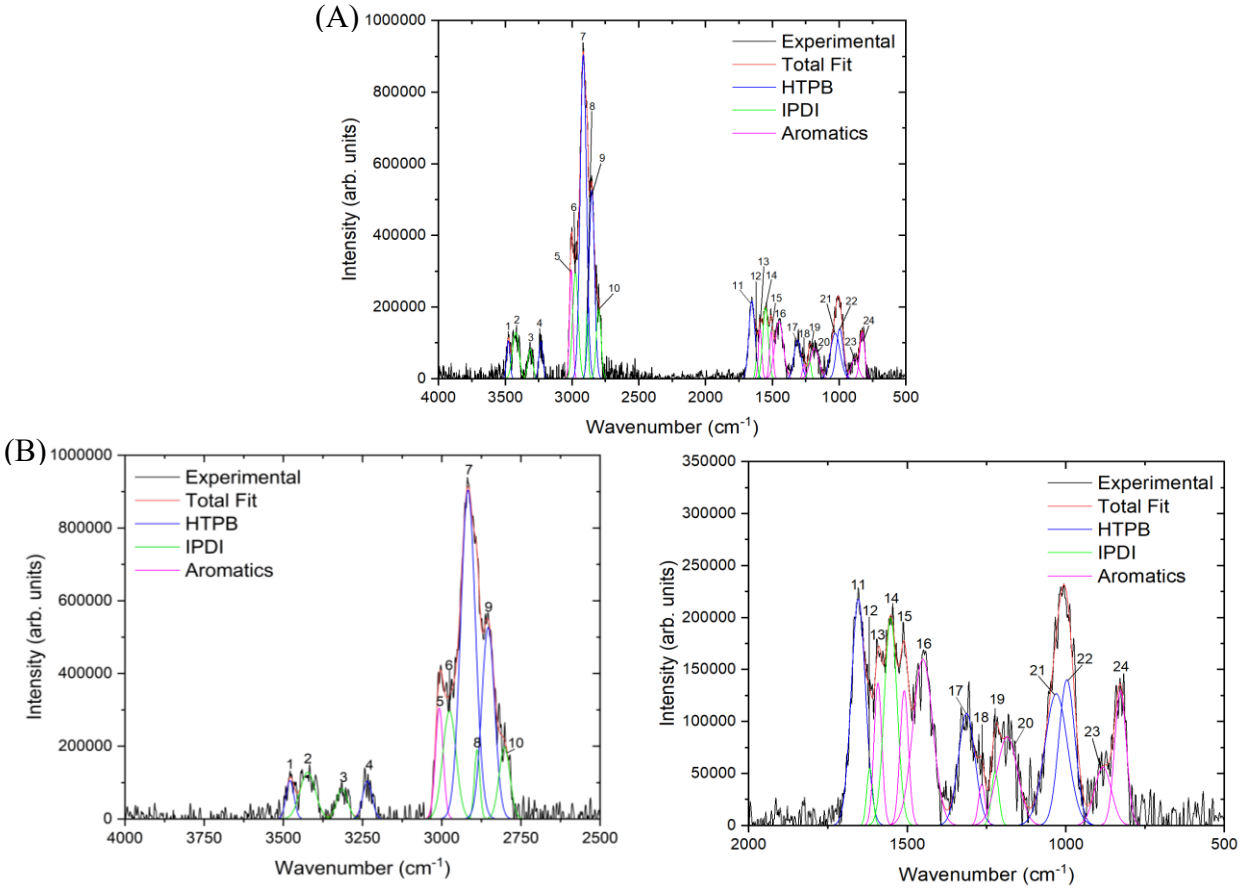

Figure S7. 587 K deconvoluted Raman spectra of HTPB in 100% Ar. (A) represents the full spectrum and (B) represents the zoomed in high and low wavenumbers of the spectrum in (A).

Table S2. Peak assignments for the deconvoluted Raman spectrum of the HTPB particle levitated in 100% Ar at 587 K.

Peaks	Experimental Frequency (cm^{-1})	Literature Frequency (cm^{-1})[1,2,4,5]	Assignment	Carrier
1	3479	3480-3270 3460-3410	ν O-H ν N-H	$-CH_2-OH$ (methanol) (unassociated) Ar-NH-CO-OR
2	3423	3410-3390 3460-3410 3450-3400	ν N-H ν_a N-H	(unassociated) -NH-CO-O- (unassociated) Ar-NH-CO-OR Primary urethane (H_2N-CO-O-)
3	3314	3410-3390	ν N-H	(unassociated) -NH-CO-O-
4	3235	3800-3000 3240-3200	ν O-H ν_s N-H	$-CH_2-OH$ Primary urethane (H_2N-CO-O-)
5	3008	3011-3004; 3003 3010 3003	ν CH	alkene (vinyl (C_4H_6) (1,3-butadiene)) aromatic (1,3-disubstituted alkyl benzene; m-xylene) aromatic (monosubstituted alkyl benzene; toluene)
6	2976	2975-2950	ν_a C-H	CH_3
7	2917	2990-2900	ν_a CH_2	$-CH_2-OH$
8	2888	2885-2865	ν_s C-H	CH_3
9	2853	2855-2845	ν_s CH_2	CH_2
10	2802	2805-2780	ν_s C-H	N-CH_3
11	1655	1645-1640; 1630; 1656	ν C=C	alkene (vinyl (C_4H_6) (1,3-butadiene))
12	1618	1630-1610	δ NH_2	urethane
13	1592	1590-1575	ν -C=C-	aromatic
14	1553	1550-1500	δ N-H	(unassociated) Ar-NH-CO-OR
15	1510	1525-1470 1600-1500	ν -C=C- δ N-H, ν C-N	aromatic secondary urethane (in solid phase)
16	1451	1480-1410 1451-1450 1436	δ CH_2 δ_s CH_2 δ CH_3	$-CH_2-OH$ CH_2 aromatic (toluene)
17	1313	1312	δ =CH	alkene

18	1265	1270-1250 1285-1235	δ C-H (in plane) ν Ar-N	aromatic N-Aryl urethane
19	1223	1260-1200	ω NH_2/CO	N-Aryl urethane
20	1173	1150-1075	ν C-O	-CH_2-OH
21	1030	1027 1030	ν C-C ring deformation	alkane cycloalkane
22	997	995-969	ω CH	alkane alkene
23	883	880-830; 890	δ C-H (out of plane)	aromatic (1,3- disubstituted alkyl benzene; m-xylene)
24	828	820-720; 843	δ C-H (out of plane)	aromatic (monosubstituted alkyl benzene; toluene)

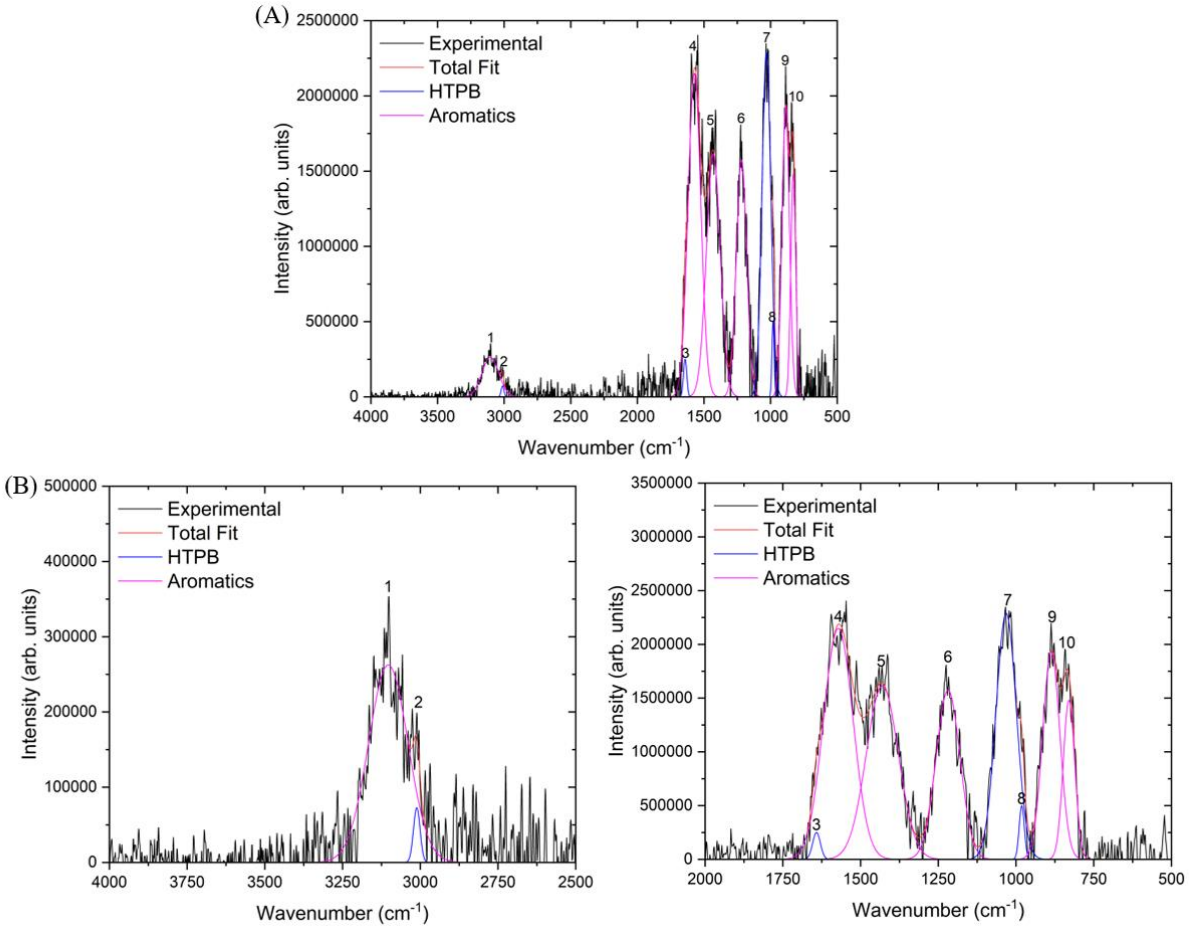

Figure S8. 718 K deconvoluted Raman spectra of HTPB in 100% Ar. (A) represents the full spectrum and (B) represents the zoomed in high and low wavenumbers of the spectrum in (A).

Table S3. Peak assignments for the deconvoluted Raman spectrum of the HTPB particle levitated in 100% Ar at 718 K.

Peaks	Experimental Frequency (cm^{-1})	Literature Frequency (cm^{-1})[1-5]	Assignment	Carrier
1	3103	3105-3000; 3086	ν =C-H	aromatic (monosubstituted alkyl benzene; toluene)
2	3011	3011-3004; 3003 3010 3003	ν CH	alkene (vinyl (C_4H_6) (1,3-butadiene)) aromatic (1,3-disubstituted alkyl benzene; m-xylene) aromatic (monosubstituted alkyl benzene; toluene)
3	1642	1645-1640; 1630	ν C=C	alkene (vinyl (C_4H_6) (1,3-butadiene))
4	1571	1590-1575	ν C=C	aromatic ring
5	1430	1436	δ CH_3	aromatic (toluene)
6	1218	1208	δ C-H (in plane)	aromatic (monosubstituted alkyl benzene; toluene)
7	1031	1027 1030	ν C-C ring deformation	alkane cycloalkane
8	981	995-969; 976	δ CH	alkene (1,3-butadiene)
9	886	880-830; 890	δ C-H (out of plane)	aromatic (1,3-disubstituted alkyl benzene; m-xylene)
10	830	820-720; 843	δ C-H (out of plane)	aromatic (monosubstituted alkyl benzene; toluene)

Table S4. FTIR peak assignments for the HTPB particle in 100% Ar. Bolded are the peaks that are hidden within the CO_2 and H_2O peaks.

Peak/Band	Experimental wavenumbers/band center (cm^{-1})	Literature wavenumbers (cm^{-1})[1,6,7,8,9,10]	Vibrational mode description*
1	4000-3500	3756, 3657	ν_s H_2O ν_{as} H_2O
2	2949	3070-2930	ν_s CH_2 (vinyl -CH=CH_2)
3	2923	2924	ν_{as} C-H (alkyl -CH_3)
4	2872	2860 2874	ν_s C-H (alkyl -CH_3)
5	2363	2362	ν_{as} CO_2 (PR)
6	**2295**	**2300-2250**	**ν_{as} R-N=C=O**
7	2255	2260	ν_{as} N_2O
8	2000-1400	1595	δ H_2O
9	**1643**	**1645-1640**	**ν C=C (vinyl (C_4H_6; 1,3 butadiene))**
10	**1453**	**1444** **1450**	**γ CH_2 (vinyl)** **δ_{as} CH (alkyl CH_3)**
11	950	950	w C-H oop (C_2H_4; ethylene)(PR)
12	668	668	δ CO_2 (Q)

*Abbreviations: ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ, bend; w, wagging; γ, scissoring; PQR, vibrational PQR branches

Table S5. FTIR peak assignments for the B/HTPB particle in 100% Ar. Bolded are the peaks that are hidden within the CO_2 and H_2O peaks.

Peak/Band	Experimental wavenumber (cm^{-1})	Literature wavenumber (cm^{-1})[1,4-10,11,12,13]	Vibrational mode description
1	4000-3500	3756 3657	ν_s H_2O ν_{as} H_2O
2	3162	3161	ν_{as} C-H (aromatic five membered ring; furan)
3	3129	3129 3140	ν_s C-H (aromatic five membered ring; furan)
4	3084	3105-3000 3083 3064	ν_{as} C-H (monosubstituted and disubstituted alkyl benzene)
5	3011	3105-3000 3012 3028	ν_s C-H (monosubstituted and disubstituted alkyl benzene)
6	2959	3070-2930	ν_s CH_2 (vinyl -CH=CH_2)
7	2923	2924	ν_{as} C-H (alkyl -CH_3)
8	2863	2860 2874	ν_s C-H (alkyl -CH_3)
9	2854	2854	ν_s C-H (aliphatic -CH_2)
10	2347	2362	ν_{as} CO_2 (PR)
11	**2300**	**2300-2250**	**ν_{as} R-N=C=O**
12	2260	2260	ν_{as} N_2O
13	2000-1400	1595	δ H_2O
14	**1721**	**1725** **1730**	**ν C=O (free)** **ν C=O (urethane)**
15	**1638**	**1645-1640**	**ν C=C (vinyl (C_4H_6) (1,3-butadiene))**
16	**1590**	**1590-1575** **1610-1560; 1556**	**ν C=C (aromatic ring)** **ν C=C (five membered ring; furan)**
17	**1499**	**1500** **1491**	**ν C-C (aromatic ring)** **ν C=C + ρ C-H (five membered ring; furan)**
18	**1450**	**1444** **1450**	**γ CH_2 (vinyl; ethylene)** **δ_{as} C-H (alkyl CH_3; toluene)**
19	**1373**	**1377** **1380**	**δ_s CH (alkyl CH_3; toluene)** **γ CH_2 (vinyl; 1,3-butadiene)**

		1384	**ρ C-H + ν C-C (five membered ring; furan)**
20	1017	1016	δ methyl CCH ip (1,3-alkyl disubstituted benzene; m-xylene)
21	993	990	ρ CH_2 (C_4H_6; 1,3-butadiene)
22	968	1010-940 995-980 966	δ C-H oop (C_4H_6; 1,3-butadiene)(PQR)
23	945	950	w C-H oop (C_2H_4; ethylene)
24	932	927 920-905	δ C=C-H oop (vinyl group) ν_s COC (five membered ring; furan)
25	909	908	w CH_2 (C_4H_6; 1,3-butadiene)(PQR)
26	876	876 871	δ C-H interior ring oop (1,3-alkyl disubstituted benzene; m-xylene) δ ring (five membered ring; furan)
27	721	770-730 728	δ C-H oop (monosubstituted alkyl benzene; toluene)
28	668	668	δ CO_2 (PQR)

*Abbreviations: ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ_{as}, asymmetric bend; δ_s, symmetric bend; w, wagging; γ, scissoring; ρ, rocking; PQR, vibrational PQR branches

Table S6. FTIR peak assignments for the HTPB particle in 20% O_2. Bolded are the peaks that are hidden within the CO_2 and H_2O peaks.

Peak/Band	Experimental wavenumber (cm^{-1})	Literature wavenumber (cm^{-1})[1,6-12,14,15,16,17]	Vibrational mode description
1	4000-3500	3756 3657	ν_s H_2O ν_{as} H_2O
2	3113	3129 3115	ν_s C-H (aromatic five membered ring; furan) ν_{as} CH_2 (methyl vinyl ether)
3	3090	3093	ν C-H (monosubstituted benzene; methoxy benzene)
4	3079	3073	ν_s C-H (methyl vinyl ether (methoxyethene))
5	3034	3035	ν C-H (monosubstituted benzene; methoxy benzene)
6	2971	3070-2930	ν_s CH_2 (vinyl -$CH=CH_2$)
7	2960	2961	ν_{as} CH_3 (methyl vinyl ether)
8	2928	2927	ν_{as} CH_3 (methyl vinyl ether (cis isomer))
9	2900	2908	ν CH (CH_3; methoxy benzene)
10	2868	2864	ν_s CH_3 (methyl vinyl ether)
11	2846	2838	ν CH (methoxy benzene (=C-O-CH_3))
12	2363	2362	ν_{as} CO_2 (PR)
13	**2313**	**2300-2250**	**ν_{as} R-N=C=O**
14	2265	2260	ν_{as} N_2O
15	**1820**	**1850-1800**	**vinyl overtone**
16	2000-1400	1595	δ H_2O
17	**1649**	**1645-1640** **1659**	**ν C=C (vinyl (C_4H_6) (1,3-butadiene))** **ν C=C (methyl vinyl ether)**
18	**1597**	**1590-1575**	**ν C=C (aromatic ring)**
19	**1568**	**1610-1560; 1556**	**ν C=C (five membered ring; furan)**

20	**1448**	**1455** **1452**	**δ_s CH_3 (vinyl; methyl vinyl ether)** **δ CH_3 (alkyl CH_3; methoxy benzene)**
21	1265	1270; 1247 1259	δ CH (methoxy benzene) ν_{as} COC (methyl vinyl ether (cis isomer))
22	1066	1066	δ CH ip (furan)
23	1043	1040	ν O-CH_3 (monosub phenyl; methoxy benzene)
24	1012	1012	ρ CH_2 (methyl vinyl ether)
25	984	990	ρ CH_2 (C_4H_6; 1,3-butadiene)
26	971	1010-940 995-980 966	δ C-H oop (C_4H_6; 1,3-butadiene)(PQR)
27	908	908	w CH_2 (C_4H_6; 1,3-butadiene)(PQR)
28	828	820-720; 825	γ C-H (monosubstituted benzene; methoxy benzene)
29	754	752	γ CH (methoxy benzene)
30	668	668	δ CO_2 (PQR)
31	525	525	δ CCO (methyl vinyl ether (cis isomer))

*Abbreviations: ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ_{as}, asymmetric bend; δ_s, symmetric bend; w, wagging; γ, scissoring; ρ, rocking; PQR, vibrational PQR branches

Table S7. FTIR peak assignments for the B/HTPB particle in 20% O_2. Bolded are the peaks that are hidden within the CO_2 and H_2O peaks.

Peak/Band	Experimental wavenumber (cm^{-1})	Literature wavenumber (cm^{-1})[1,6-12,15-18,19,20]	Vibrational mode description
1	4000-3500	3756 3657	ν_s H_2O ν_{as} H_2O
2	3705	3687	ν OH (methanol)(PQR)
3	3112	3129 3115	ν_s C-H (aromatic five membered ring; furan) ν_{as} CH_2 (methyl vinyl ether)
4	3082	3076 3073	ν C-H (monosubstituted benzene; nitrobenzene) ν_s C-H (methyl vinyl ether (methoxyethene))
5	3035	3035	ν C-H (monosubstituted benzene; nitrobenzene)
6	2998	3070-2930; 2984	ν_s CH_2 (vinyl -$CH=CH_2$; 1,3-butadiene)
7	2968	2960 2961	ν_s CH_3 (methanol) ν_{as} CH_3 (methyl vinyl ether)
8	2926	2927	ν_{as} CH_3 (methyl vinyl ether (cis isomer))
9	2868	2864 2869	ν_s CH_3 (methyl vinyl ether) ν_s CH_3 (methanol (R))
10	2840	2844	ν_s CH_3 (methanol (PQ))
11	2363	2362	ν_{as} CO_2 (PR)
12	**2332**	**2300-2250**	**ν_{as} R-N=C=O**
13	2260	2260	ν_{as} N_2O
14	2000-1400	1595	δ H_2O
15	**1648**	**1645-1640** **1659**	**ν C=C (vinyl (C_4H_6) (1,3-butadiene))** **ν C=C (methyl vinyl ether)**
16	**1594**	**1590-1575** **1610-1560; 1556** **1612**	**ν C=C (aromatic ring)** **ν C=C (five membered ring; furan)** **ν_{as} NO_2 (free)**
17	**1514**	**1570-1490; 1527**	**ν NO_2 (nitrobenzene)**
18	**1500**	**1500**	**ν C-C (aromatic ring)**

		1491	**ν C=C + ρ C-H (five membered ring; furan)**
19	**1430**	**1430**	**δ_{as} CH_3 (alkyl CH_3; methanol)**
20	**1363**	**1390-1300, 1351** **1380** **1384** **1345**	**ν NO_2 (nitrobenzene)** **γ CH_2 (vinyl; 1,3-butadiene)** **ρ C-H + ν C-C (five membered ring; furan)** **δ OH (methanol)**
21	**1295**	**1294**	**δ CH (1,3-butadiene)**
22	1062	1066 1060	δ CH ip (furan) ρ CH_3 (methanol)
23	1035	1033	ν CO (methanol)
24	1005	1004	δ CCC (nitrobenzene)
25	971	1010-940 995-980 966	δ C-H oop (C_4H_6; 1,3-butadiene)(PQR)
26	934	935	γ CH (nitrobenzene)
27	908	908	w CH_2 (C_4H_6; 1,3-butadiene)(PQR)
28	876	871	δ ring (five membered ring; furan)
29	668	668	δ CO_2 (PQR)

*Abbreviations: ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ_{as}, asymmetric bend; δ_s, symmetric bend; w, wagging; γ, scissoring; ρ, rocking; PQR, vibrational PQR branches

Table S8. Peak assignments for the deconvoluted emission spectrum of the B/HTPB particle levitated in 20% O_2 and 80% Ar.

Peak/band	Peak wavelength/band center (nm)	Reference wavelength (nm)[21,22,23,24]	Carrier	Transition	Branch; spin-orbit components; vibrational quantum numbers: (ν', ν") or (ν1',ν2',ν3') – (ν1",ν2",ν3")
1	210	208	B	$2p^2\ ^2D – 2p\ ^2P^o$	5/2 – 3/2
2	408	409 403	BO_2 BO	B $^2\Sigma^+u$ – X $^2\Pi g$ A $^2\Pi$–X $^2\Sigma^+$	(0,0); (1,1); (2,2) (1,0)
3	430	425 434	BO BO_2	A $^2\Pi$–X $^2\Sigma^+$ A $^2\Pi u$ – X $^2\Pi g$	(0,0) (0,2,n)-(0,0,n); (0,3,n)-(1,1,n)
4	436	437	BO	A $^2\Pi$–X $^2\Sigma^+$	(1,1)
5	454	452	BO BO_2	A $^2\Pi$–X $^2\Sigma^+$ A $^2\Pi u$ – X $^2\Pi g$	(0,1) (n,2,m)-(n-2,2,m); (n,3,0)-(n-1,3,m)
6	474	474	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(n,2,m)-(n-1,2,m); (n,1,m)-(n-2,1,m)
7	481	480, 474	C_2	d $^3\Pi g$ - a $^3\Pi u$	(1,0)
8	494	495	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(n,0,m)-(n-2,0,m); (n,1,m)-(n-1,1,m)
9	505	505	C_2	d $^3\Pi g$ - a $^3\Pi u$	(3,3)
10	518	520 516	BO_2 C_2	A $^2\Pi u$ – X $^2\Pi g$ d $^3\Pi g$ - a $^3\Pi u$	(n,0,m)-(n-1,0,m); (n,1,m)-(n,1,m) (0,0)
11	548	548	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(n,0,m)-(n,0,m)
12	549	549 551	C_2 BO	d $^3\Pi g$ - a $^3\Pi u$ A $^2\Pi$–X $^2\Sigma^+$	(3,4) (0,3)
13	581	581 582	BO_2 B	A $^2\Pi u$ – X $^2\Pi g$ 3d $^2D^o$ – $2p^2\ ^2P$	(n,0,m)-(n+1,0,m) 5/2 – 3/2
14	589	588	Na	3p $^2P^o$ – 3s ^2S	3/2 – 1/2
15	598	589, 596	Na	3p $^2P^o$ – 3s ^2S	1/2 – 1/2
16	623	623	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(n,0,m)-(n+2,0,m)
17	641	641	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(n,0,m)-(n+3,0,m)
18	660	670	Li	2p $^2P^o$ – 2s ^2S	3/2 – 1/2
19	680	682	BO_2	A $^2\Pi u$ – X $^2\Pi g$	(0,0,m)-(1,2,m)
20	744	741	BO	A $^2\Pi$–X $^2\Sigma^+$	(1,6)
21	755	757	BO	A $^2\Pi$–X $^2\Sigma^+$	(2,7)
22	768	766	K	4p $^2P^o$ – 4s ^2S	3/2 – 1/2
23	773	769	K	4p $^2P^o$ – 4s ^2S	1/2 – 1/2
24	802	806	BO	A $^2\Pi$–X $^2\Sigma^+$	(0,6)
25	822	820	Na	3d ^2D – 3p $^2P^o$	5/2 – 3/2

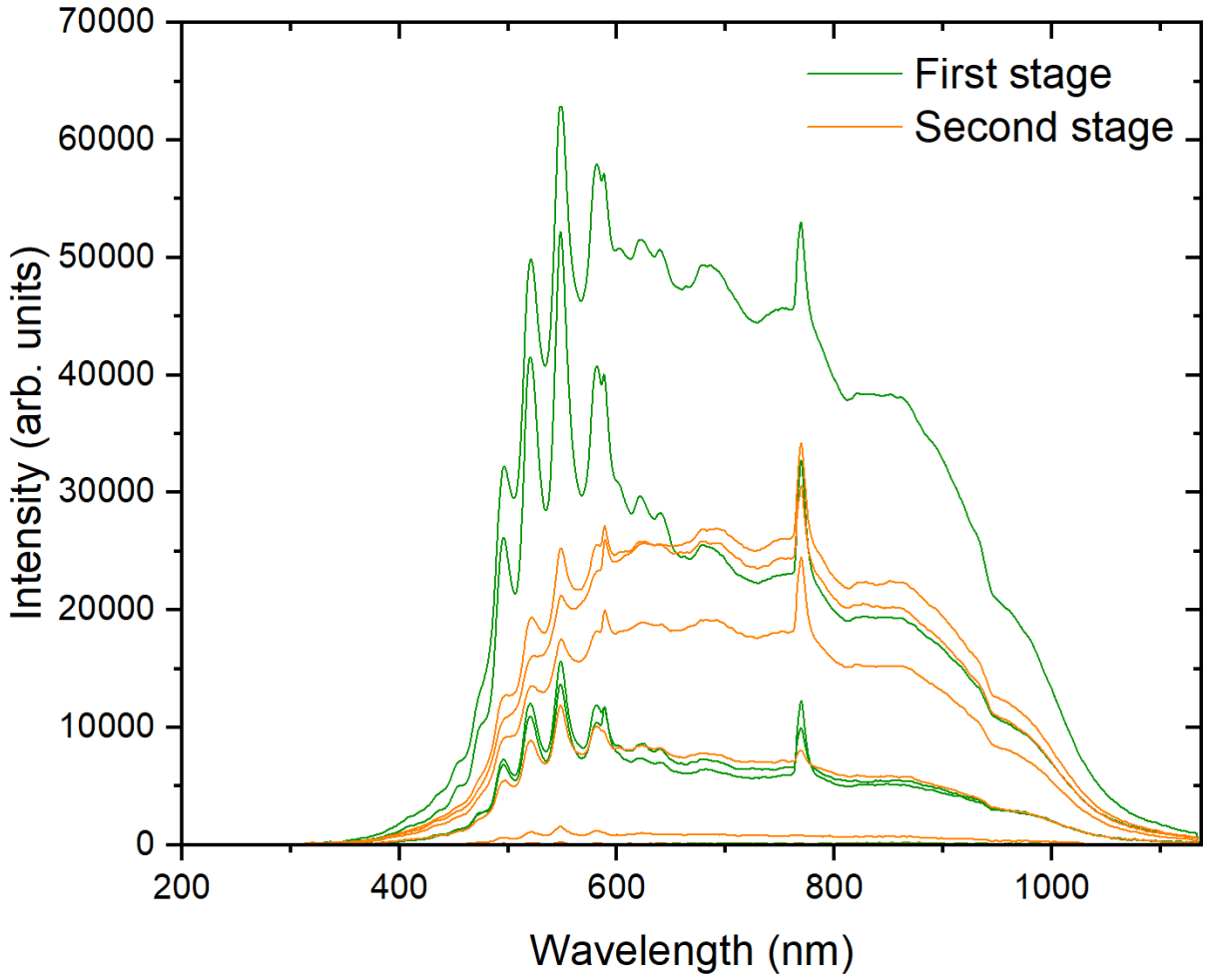

Figure S9. 2D plot of the B/HTPB emission spectra when levitated in 20% O_2 and 80% Ar.

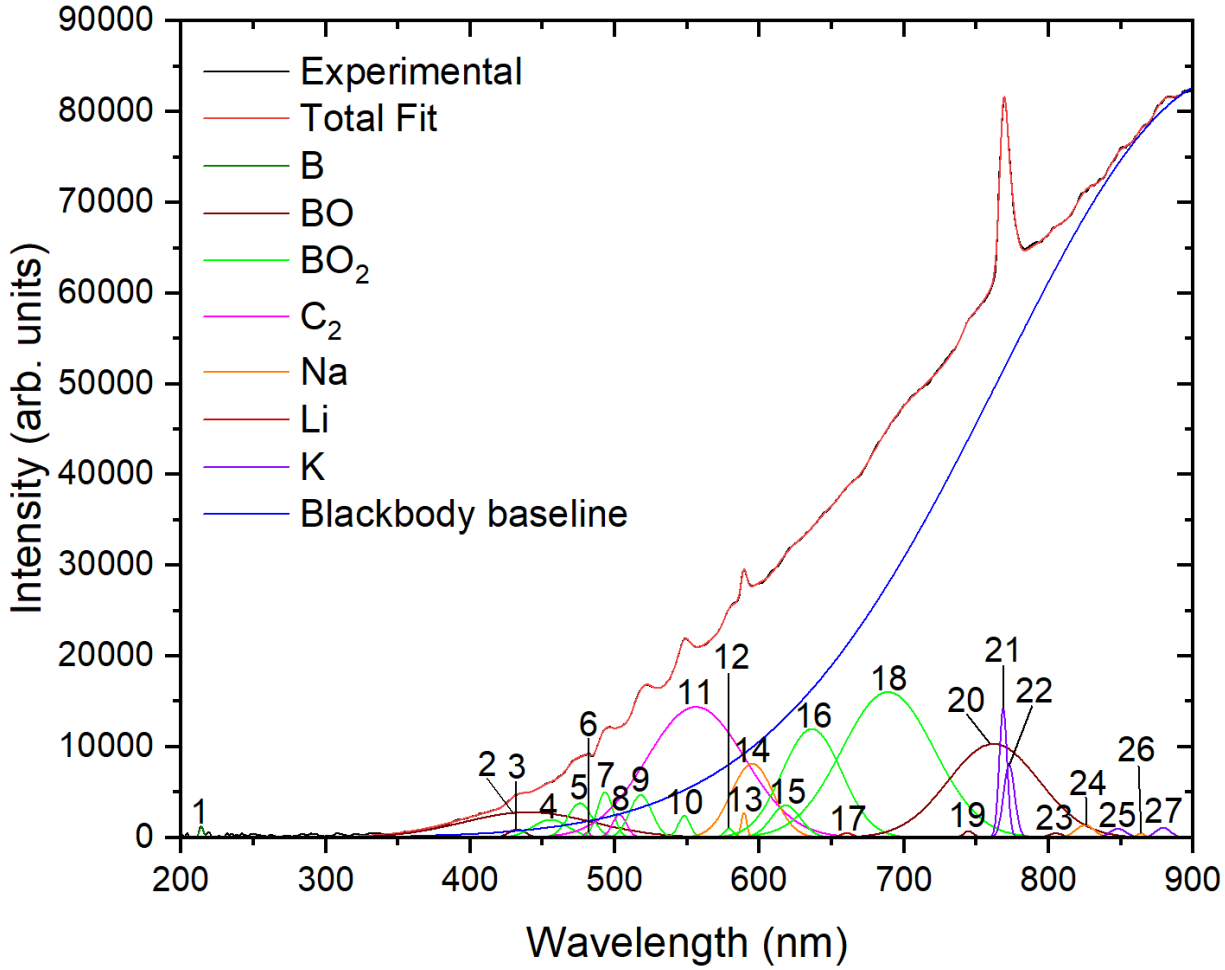

Figure S10. Deconvoluted UV-Vis emission spectrum of the levitated B/HTPB particle during the second stage of ignition in 20% O_2 and 80% Ar.

Table S9. Peak assignments for the deconvoluted emission spectrum during the second stage of ignition for the B/HTPB particle levitated in 20% O_2 and 80% Ar.

Peak/band	Peak wavelength/band center (nm)	Reference wavelength (nm)[22-25]	Carrier	Transition	Branch; spin-orbit components; vibrational quantum numbers: (ν', ν") or (ν1',ν2',ν3') – (ν1",ν2",ν3")
1	210	208	B	$2p^2\ ^2D – 2p\ ^2P^o$	5/2 – 3/2
2	432	425 434	BO BO_2	$A\ ^2\Pi – X\ ^2\Sigma^+$ $A\ ^2\Pi u – X\ ^2\Pi g$	(0,0) (0,2,n)-(0,0,n); (0,3,n)-(1,1,n)
3	439	437	BO	$A\ ^2\Pi – X\ ^2\Sigma^+$	(1,1)
4	455	452	BO BO_2	$A\ ^2\Pi – X\ ^2\Sigma^+$ $A\ ^2\Pi u – X\ ^2\Pi g$	(0,1) (n,2,m)-(n-2,2,m); (n,3,0)-(n-1,3,m)
5	475	474	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(n,2,m)-(n-1,2,m); (n,1,m)-(n-2,1,m)
6	481	480, 474	C_2	$d\ ^3\Pi g - a\ ^3\Pi u$	(1,0)
7	493	495	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(n,0,m)-(n-2,0,m); (n,1,m)-(n-1,1,m)
8	503	505	C_2	$d\ ^3\Pi g - a\ ^3\Pi u$	(3,3)
9	518	520 516	BO_2 C_2	$A\ ^2\Pi u – X\ ^2\Pi g$ $d\ ^3\Pi g - a\ ^3\Pi u$	(n,0,m)-(n-1,0,m); (n,1,m)-(n,1,m) (0,0)
10	548	548	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(n,0,m)-(n,0,m)
11	556	549 551	C_2 BO	$d\ ^3\Pi g - a\ ^3\Pi u$ $A\ ^2\Pi – X\ ^2\Sigma^+$	(3,4) (0,3)
12	579	581 582	BO_2 B	$A\ ^2\Pi u – X\ ^2\Pi g$ $3d\ ^2D^o – 2p^2\ ^2P$	(n,0,m)-(n+1,0,m) 5/2 – 3/2
13	589	588	Na	$3p\ ^2P^o – 3s\ ^2S$	3/2 – 1/2
14	595	589, 596	Na	$3p\ ^2P^o – 3s\ ^2S$	1/2 – 1/2
15	618	623	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(n,0,m)-(n+2,0,m)
16	636	641	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(n,0,m)-(n+3,0,m)
17	660	670	Li	$2p\ ^2P^o – 2s\ ^2S$	3/2 – 1/2
18	689	682	BO_2	$A\ ^2\Pi u – X\ ^2\Pi g$	(0,0,m)-(1,2,m)
19	745	741	BO	$A\ ^2\Pi – X\ ^2\Sigma^+$	(1,6)
20	762	757	BO	$A\ ^2\Pi – X\ ^2\Sigma^+$	(2,7)
21	769	766	K	$4p\ ^2P^o – 4s\ ^2S$	3/2 – 1/2
22	773	769	K	$4p\ ^2P^o – 4s\ ^2S$	1/2 – 1/2
23	805	806	BO	$A\ ^2\Pi – X\ ^2\Sigma^+$	(0,6)
24	825	820	Na	$3d\ ^2D – 3p\ ^2P^o$	5/2 – 3/2
25	848	850	K	$8f\ ^2F^o – 3d\ ^2D$	5/2 – 5/2
26	864	864	Na	$6p\ ^2P^o – 4s\ ^2S$	3/2 – 1/2
27	879	876	K	$9p\ ^2P^o – 3d\ ^2D$	3/2 – 5/2

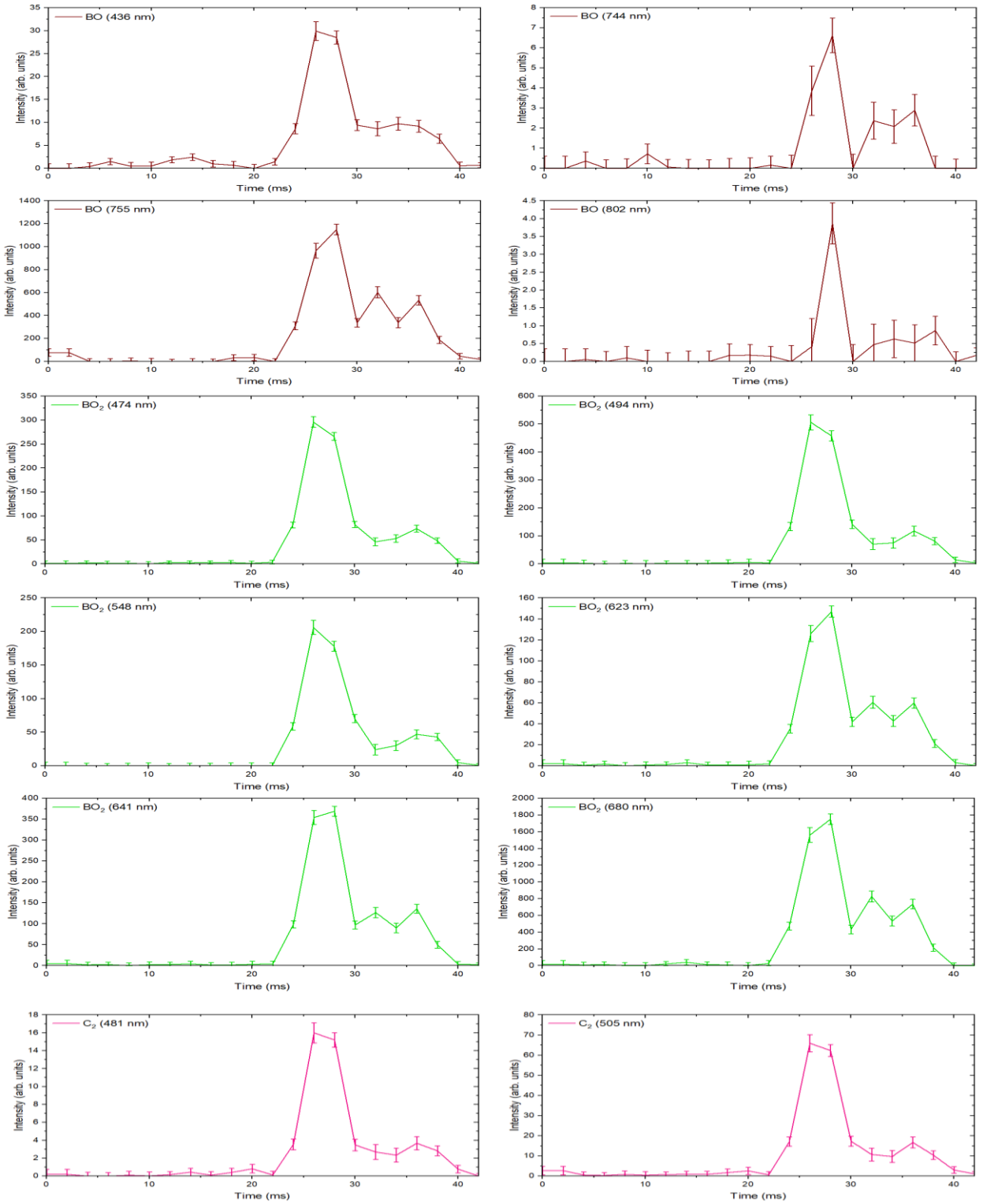

Figure S11. Emission profiles from the individual peaks from selected species (BO, BO_2, C_2) in B/HTPB levitated in 20% O_2 and 80% Ar.

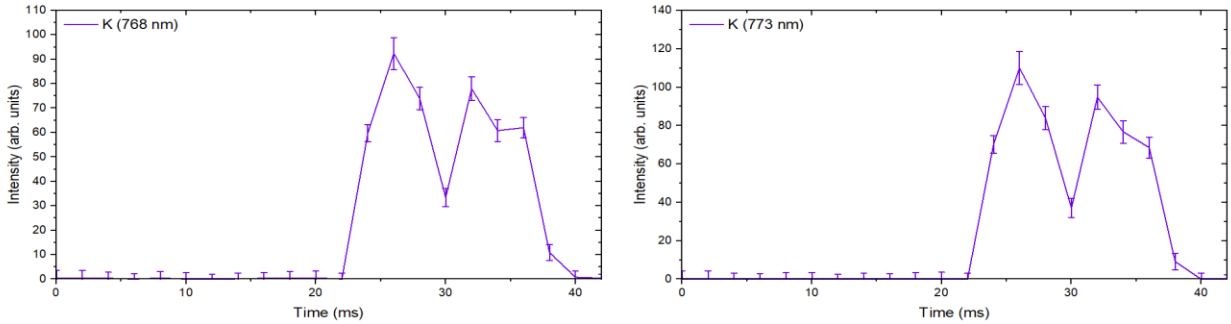

Figure S12. Emission profiles from the individual K peaks in B/HTPB levitated in 20% O_2 and 80% Ar.

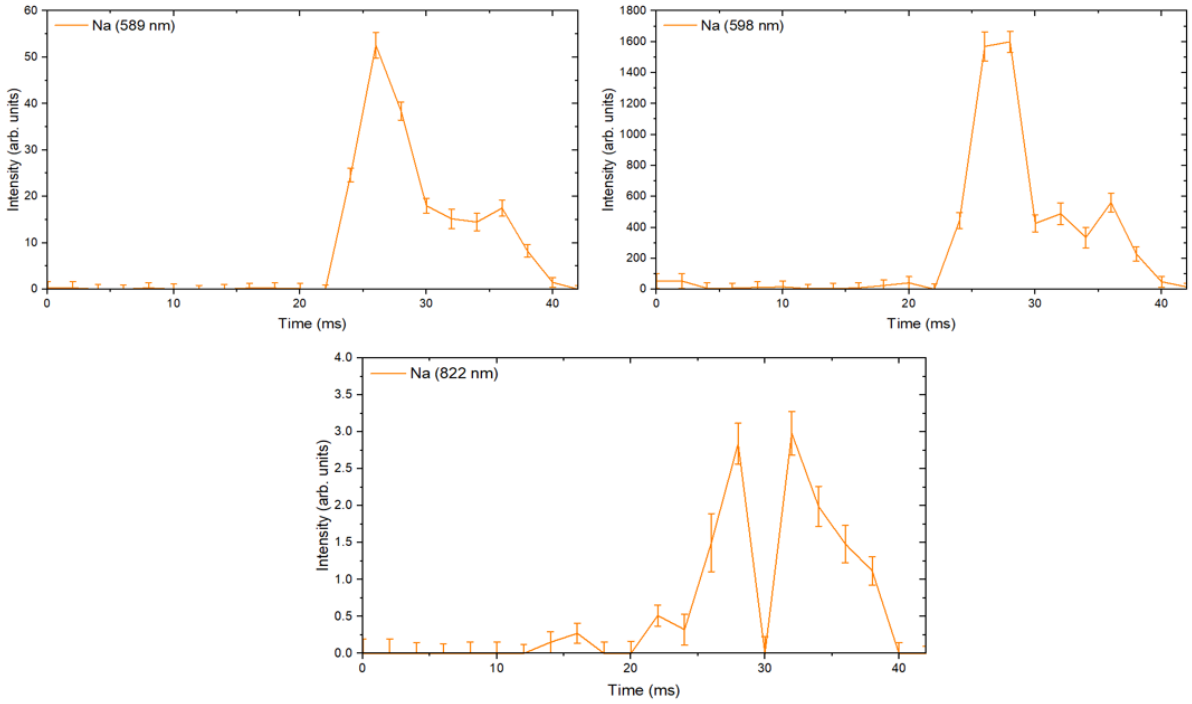

Figure S13. Emission profiles from the individual Na peaks in B/HTPB levitated in 20% O_2 and 80% Ar.

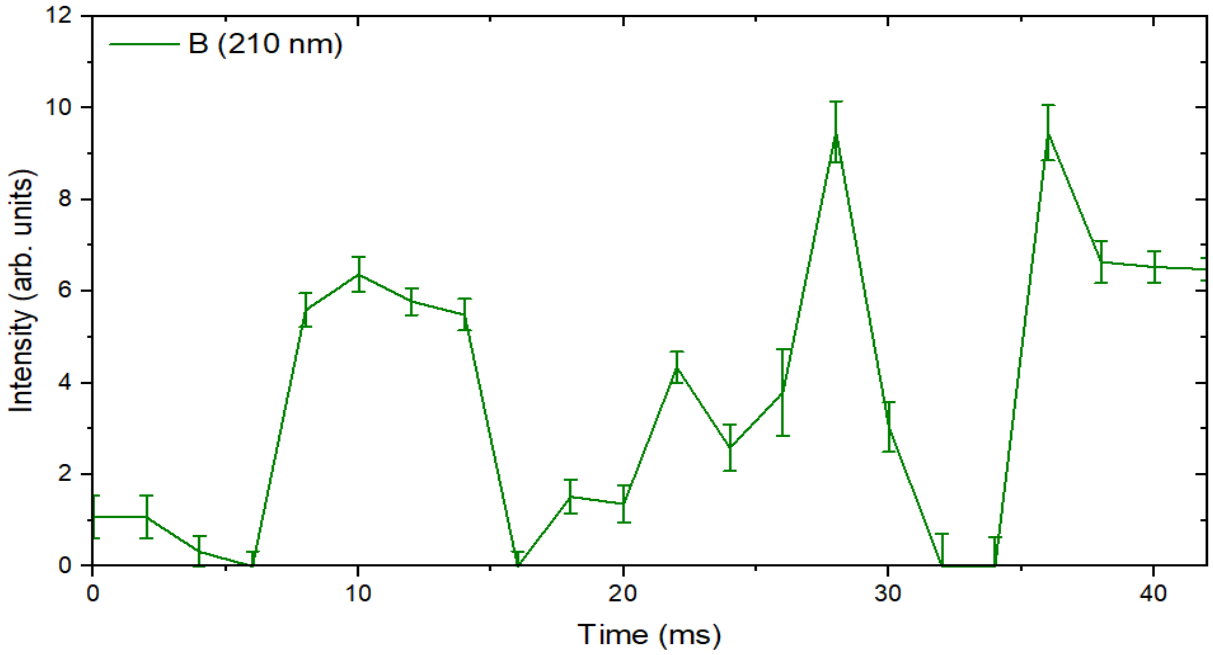

Figure S14. Emission profile from the individual B peak in B/HTPB levitated in 20% O_2 and 80% Ar.

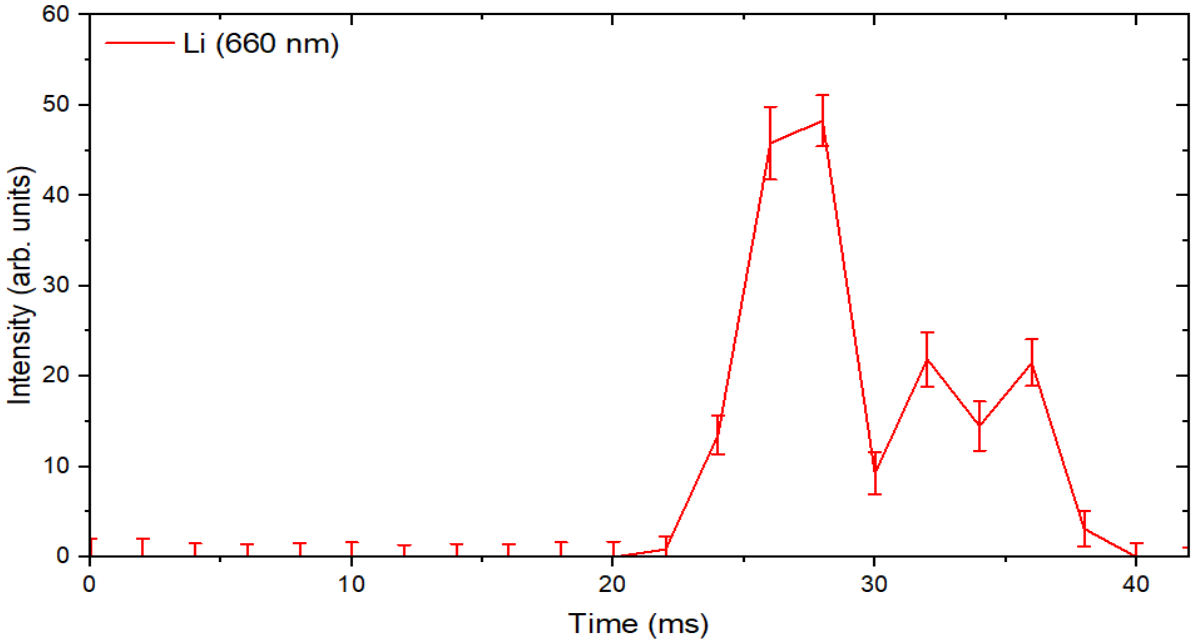

Figure S15. Emission profile from the individual Li peak in B/HTPB levitated in 20% O_2 and 80% Ar.

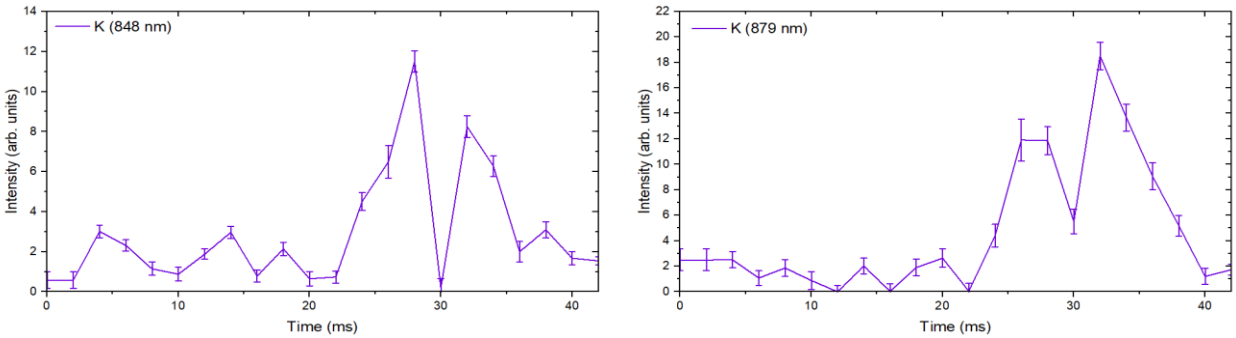

Figure S16. Emission profiles from the individual K peaks in B/HTPB levitated in 20% O_2 and 80% Ar in the second stage of the ignition.

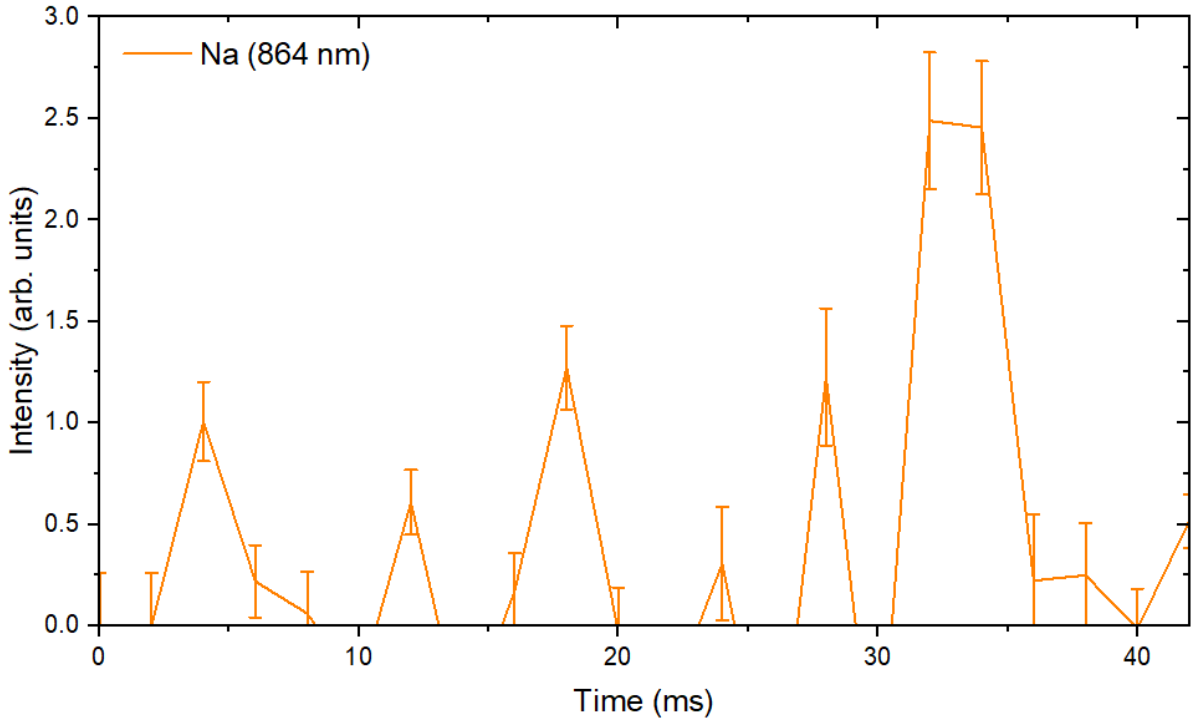

Figure S17. Emission profile from the individual Na peak in B/HTPB levitated in 20% O_2 and 80% Ar in the second stage of the ignition.

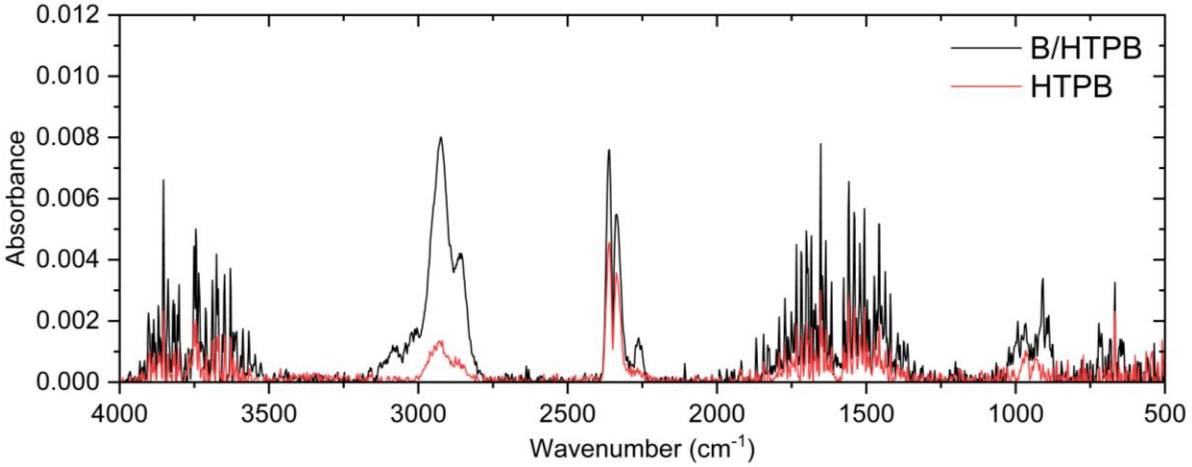

Figure S18. Combined gas phase FTIR spectra of B/HTPB and HTPB in 100% Ar.

References

(1) Socrates, G. *Infrared and Raman Characteristic Group Frequencies : Tables and Charts*, Third.; John Wiley & Sons, Ltd: England, Chichester, 2001.

(2) Cornell, S. W.; Koenig, J. L. The Raman Spectra of Polybutadiene Rubbers. *Macromolecules* **1969**, *2* (5), 540–545.

(3) Nallasamy, P.; Anbarasan, P. M.; Mohan, S. Vibrational Spectra and Assignments of Cis- and Trans-1,4-Polybutadiene *. *Turk J Chem* **2002**, *26*, 105–111.

(4) Wilmshurst, J. K.; Bernstein, H. J. THE INFRARED AND RAMAN SPECTRA OF TOLUENE, TOLUENE-α-D3, m-XYLENE, AND m-XYLENE-Aα′-D6. *Can. J. Chem.* **1957**, *35*, 911–925.

(5) Lindenmaier, R.; Scharko, N. K.; Tonkyn, R. G.; Nguyen, K. T.; Williams, S. D.; Johnson, T. J. Improved Assignments of the Vibrational Fundamental Modes of Ortho-, Meta-, and Para-Xylene Using Gas- and Liquid-Phase Infrared and Raman Spectra Combined with Ab Initio Calculations: Quantitative Gas-Phase Infrared Spectra for Detection. *J. Mol. Struct.* **2017**, *1149*, 332–351.

(6) Chen, J. K.; Brill, T. B. Chemistry and Kinetics of Hydroxyl-Terminated Polybutadiene (HTPB) and Diisocyanate-HTPB Polymers during Slow Decomposition and Combustion-like Conditions. *Combust. Flame* **1991**, *87* (3–4), 217–232.

(7) Liang, J.; Nie, J.; Zhang, H.; Guo, X.; Yan, S.; Han, M. Interaction Mechanism of Composite Propellant Components under Heating Conditions. *Polym. 2023, Vol. 15, Page 2485* **2023**, *15* (11), 2485.

(8) Craig, N. C.; Davis, J. L.; Hanson, K. A.; Moore, M. C.; Weidenbaum, K. J.; Lock, M. Analysis of the Rotational Structure in Bands in the High-Resolution Infrared Spectra of Butadiene and Butadiene-2,3-D2: Refinement in Assignments of Fundamentals. *J. Mol. Struct.* **2004**, *695–696*, 59–69.

(9) Ducruet, N.; Delmotte, L.; Schrodj, G.; Stankiewicz, F.; Desgardin, N.; Vallat, M. F.; Haidar, B. Evaluation of Hydroxyl Terminated Polybutadiene-Isophorone Diisocyanate Gel Formation During Crosslinking Process. *J. Appl. Polym. Sci.* **2013**, *128* (1), 436–443.

(10) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*; National Bureau of Standards, 1972.

(11) Burcl, R.; Handy, N. C.; Carter, S. Vibrational Spectra of Furan, Pyrrole, and Thiophene from a Density Functional Theory Anharmonic Force Field. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2003**, *59* (8), 1881–1893.

(12) Cataliotti, R.; Paliani, G. Infrared Study of the C-H Stretching Region of Five-Membered Heterocyclic Compounds. *Can. J. Chem.* **1976**, *54*, 2451–2457.

(13) Margoshes, M.; Fassel, V. A. The Infrared Spectra of Aromatic Compounds: I. The out-of-Plane C-H Bending Vibrations in the Region 625–900 Cm−1. *Spectrochim. Acta* **1955**, *7* (C), 14–24.

(14) Owen, N. L.; Hester, R. E. Vibrational Spectra and Torsional Barriers of Anisole and Some Monohalogen Derivatives. *Spectrochim. Acta Part A Mol. Spectrosc.* **1969**, *25* (2), 343–354.

(15) Stephenson, C. V.; Coburn, W. C.; Wilcox, W. S. The Vibrational Spectra and Assignments of Nitrobenzene, Phenyl Isocyanate, Phenyl Isothiocyanate, Thionylaniline and Anisole. *Spectrochim. Acta* **1961**, *17* (9–10), 933–946.

(16) Ignatyev, I. S.; Lazarev, A. N.; Smirnov, M. B.; Alpert, M. L.; Trofimov, B. A. Vibrational Spectra and Molecular Structure of Methyl Vinyl Ether. *J. Mol. Struct.* **1981**, *72* (C), 25–39.

(17) Ignatyev, I. S.; Montejo, M.; Sundius, T.; Partal Ureña, F.; López González, J. J. Structure and Vibrational Spectra of Vinyl Ether Conformers. The Comparison of B3LYP and MP2 Predictions. *Chem. Phys.* **2007**, *333* (2–3), 148–156.

(18) Falk, M.; Whalley, E. Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases. *J. Chem. Phys.* **1961**, *34* (5), 1554–1568.

(19) Clarkson, J.; Smith, W. E. A DFT Analysis of the Vibrational Spectra of Nitrobenzene. *J. Mol. Struct.* **2003**, *655* (3), 413–422.

(20) Laane, J.; Ohlsen, J. R. *Characterization of Nitrogen Oxides by Vibrational Spectroscopy*; Lippard, S. J., Ed.; John Wiley & Sons, Ltd, 1980.

(21) Hashim, S. A.; Karmakar, S.; Roy, A. Combustion Characteristics of Boron-HTPB-Based Solid Fuels for Hybrid Gas Generator in Ducted Rocket Applications. *Combust. Sci. Technol.* **2019**, *191* (11), 2082–2100.

(22) Brotton, S. J.; Perera, S. D.; Misra, A.; Kleimeier, N. F.; Turner, A. M.; Kaiser, R. I.; Palenik, M.; Finn, M. T.; Epshteyn, A.; Sun, B. J.; Zhang, L. J.; Chang, A. H. H. Combined Spectroscopic and Computational Investigation on the Oxidation of Exo-Tetrahydrodicyclopentadiene (JP-10; C10H16) Doped with Titanium–Aluminum–Boron Reactive Metal Nanopowder. *J. Phys. Chem. A* **2022**, *126* (1), 125–144.

(23) Biswas, S.; Fujioka, K.; Antonov, I.; Rizzo, G. L.; Chambreau, S. D.; Schneider, S.; Sun, R.; Kaiser, R. I. Hypergolic Ionic Liquids: To Be or Not to Be? *Chem. Sci.* **2024**, *15* (4), 1480–1487.

(24) Antonov, I.; Chyba, A.; Perera, S. D.; Turner, A. M.; Pantoya, M. L.; Finn, M. T.; Epshteyn, A.; Kaiser, R. I. Discovery of Discrete Stages in the Oxidation of Exo-Tetrahydrodicyclopentadiene (C10H16) Droplets Doped with Titanium-Aluminum-Boron Reactive Mixed-Metal Nanopowder. *J. Phys. Chem. Lett.* **2022**, *13* (41), 9777–9785.