Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.
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Supporting Information for

Correlation of molecular, atomic emissions with detonation parameters in femtosecond and nanosecond LIBS plasma of novel high energy materials

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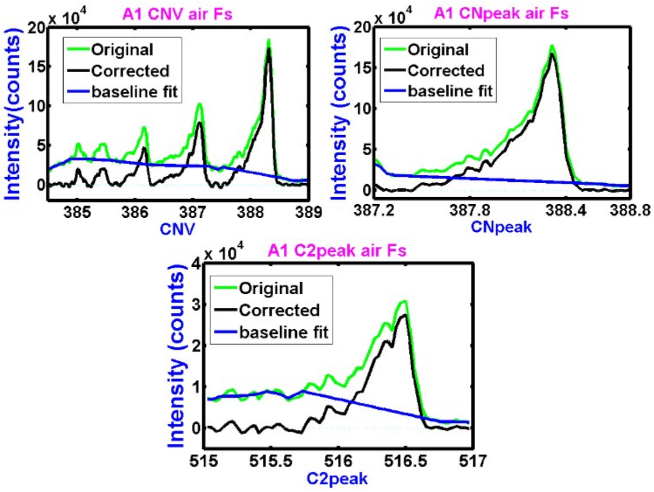
1. **Figure-1 depicting back ground corrected data obtained for CN and C_2 emissions using MATLAB programme.**



2. **Table-1 illustrating the BDE calculations obtained with Gaussian software.**

Density Functional Theory (DFT) has been used to optimize all the structures at the B3LYP level together with 6-311G++ (d, p) basis set by using Gaussian 09 package. The BDEs of C-CH_3, C-OCH_3, C-NH_2 at para and ortho positions are estimated by calculating total energy of the molecule.

The BDE is defined as the difference between the zero-point energy of the parent molecule in gas phase and those of the corresponding radicals in the unimolecular bond dissociation at 298.15 K.

Method we followed

The Total energy (the electronic energy and thermal energy) of a complete molecule (A) and with bond removed at ortho or para position (B) are calculated. The BDE is found by subtracting total energy of A from B.

Total energy of molecule with bond ruptured at para position = -881.6980 Hartree

Total energy of molecule with bond ruptured at Ortho position = -881.6992 Hartree

1 Hartree= 2625.5 KJ/mol^{-1}.

1	2	3	4	5	6
	Para / ortho removed (B)	Complete molecule (A)	BDE = B-A (Hartree) (col3-col2)	Difference (Ortho-para) (Hartree)	BDE (KJmol^{-1})
A1 C-CH_3 (p)	-881.6980	-921.6716	39.9736	0.0016	4.2
A4 C- CH_3 (o)	-881.69992	-921.6744	39.9752		
A2 C-OCH_3 (p)	-881.6980	-996.8836	115.185	0.008	21.0
A5 C-OCH_3 (o)	-881.69992	-996.8931	115.193		
A3 C-NH_2 (p)	-881.6980	-937.7123	56.0143	0.0404	106.07
A6 C-NH_2 (o)	-881.69992	-937.7539	56.0547		

Difference in BDE between ortho and para isomers is highest for –NH_2 group and is attributed to maximum stabilization arising from H bonding (both intra and intermolecular).

3. Thermodynamics of CN, C_2 pathways

Seven pathways in total resulting in CN and C_2molecular emissions are shown below and their standard enthalpy of reaction (ΔH^{o}_{rxn}), standard Gibbs free energy of reaction (ΔG^{o}_{rxn}) and the equilibrium constants, K_{eq} for all reactions at four different temperatures 3000 K, 4000 K, 5000 K, 6000 K are tabulated.

Enthalpy is a state function and standard enthalpy change of formation for a reaction can be calculated by using the below equation.

$$\Delta H^{0}_{reaction} = \Sigma \Delta H^{0}_{f}(\text{products}) - \Sigma \Delta H^{0}_{f}(\text{Reactants})$$

In analogous way, standard Gibbs free energy of a reaction can also be calculated.

$$\Delta G^{0}_{reaction} = \Sigma \Delta G^{0}_{f}\ (\text{products}) - \Sigma \Delta G^{0}_{f}\ (\text{Reactants})$$

The equilibrium constant K_{eq} for the process at that temperature is obtained using the relationship $K_{eq} = e^{-\Delta G^0/RT}$

The seven reactions stated in manuscript are:

$C + N \rightarrow CN$ (1)

$C + N_2 \rightarrow CN + N$ (2)

$C_2 + N \rightarrow CN + C$ (3)

$C_2 + N_2 \rightarrow 2CN$ (4)

$C_2 + O \rightarrow CO + C$ (5)

$C_2 + O_2 \rightarrow 2CO$ (6)

$C + C + M \rightarrow C_2 + M$ (7)

In Thermodynamics, ΔG_{rxn}, plays a crucial role in deciding the spontaneity of reaction. If $\Delta G>0$ the reaction is non-spontaneous; $\Delta G=0$ the reaction reaches equilibrium; $\Delta G<0$ the reaction is spontaneous (products are favored).

Reactions 1, 3, 5, 6,7 are exothermic in nature ($\Delta H<0$) and reactions 2 and 4 are endothermic in nature ($\Delta H>0$) (see Table 2)

	ΔH (kJ/mol)				ΔG(kJ/mol)				K_{eq}			
Reaction	**3000 K**	**4000 K**	**5000 K**	**6000 K**	**3000 K**	**4000 K**	**5000 K**	**6000 K**	**3000 K**	**4000 K**	**5000 K**	**6000 K**
(1)	-769.854	-769.483	-769.025	-770.387	-387.964	-260.682	-133.559	930.927	5692424	2536.767	24.8503	1.136367
(2)	195.232	200.919	208.799	218.311	169.928	160.708	149.781	210.979	0.001099	0.007967	0.027239	0.064023
(3)	-164.126	-161.697	-159.71	-160.607	-159.277	-157.994	-157.339	-1090.64	593.4158	115.6816	44.03202	23.19865
(4)	31.106	39.222	49.089	57.704	10.651	2.714	-7.558	-879.658	0.652444	0.921632	1.199391	1.485242
(5)	-490.36	-493.924	-498.682	-505.07	-440.189	-422.954	-404.691	-722.128	46200655	333742.8	16901.7	2262.805
(6)	-1072.97	-1080.64	-1090.64	-1103.26	-1000.41	-975.136	-947.652	528.219	2.63E+17	5.43E+12	7.95E+09	98058077
(7)	-605.728	-607.786	-609.315	-609.78	-228.687	-102.688	23.78	2021.564	9592.641	21.92886	0.564369	0.048984

Table 2. The Standard enthalpy change (ΔH_r), and Gibbs free energy change (ΔG_r), and equilibrium constant (K_{eq}) for the proposed reaction channels (1 – 7) listed above