AVT-340 Research Workshop on Preparation and Characterization of Energetic Materials

Screening the next cooling additives for gun propellant via quantum chemical calculations

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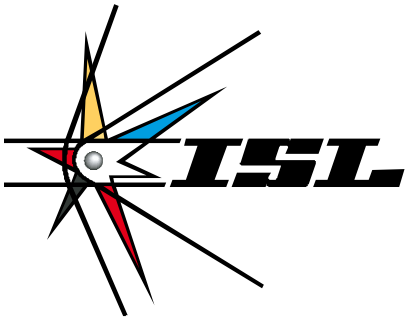
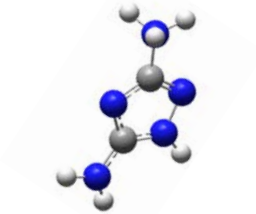
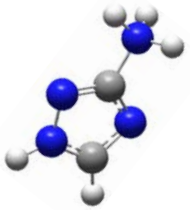
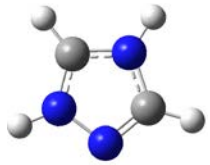


Summary

- Introduction
- Theoretical approach
- Validation
- Results
- Conclusion



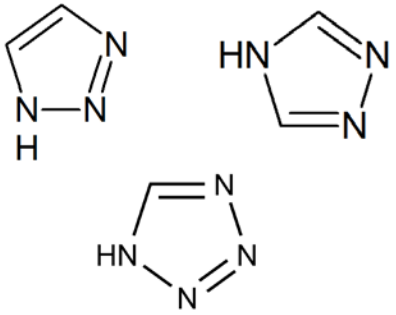




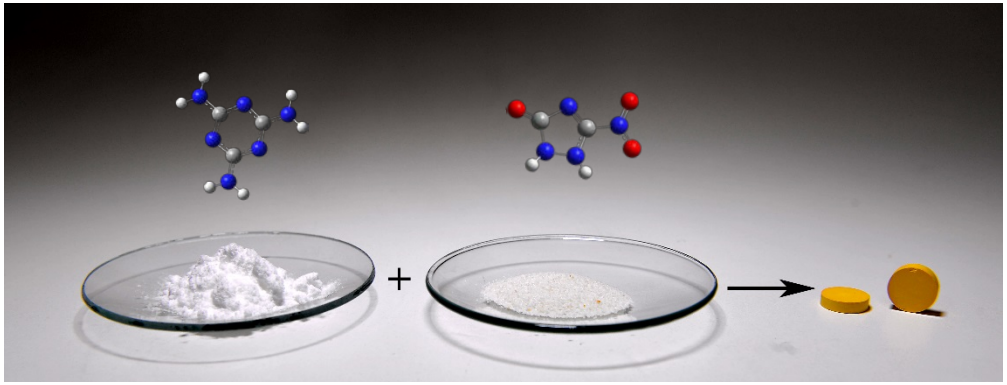
Introduction

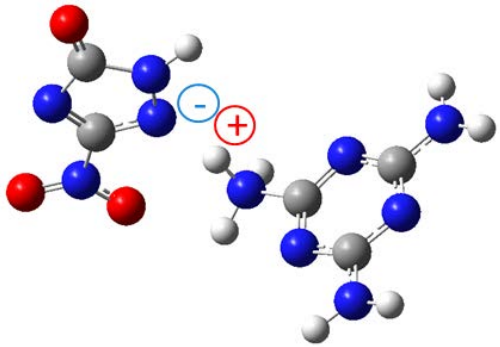
- **New generation of <u>gun propellant</u> = Extended list of requirements (Performances, REACH, LOVA, green, …)**

- **Suitable candidate : Azole-based Salts**

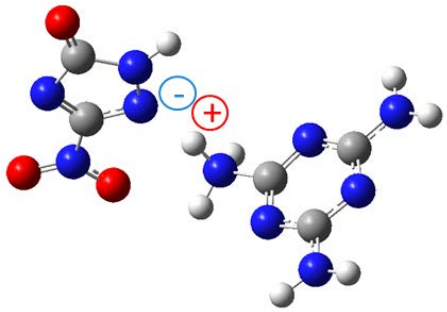


- **Home made synthesis: one step reaction**





Introduction



- **Why azole-based salts are suitable candidates ?**

Safe EM

- Highly insensitive to impact (IS) and friction
- IS can reach more than 30 J (IS = 7.4 J for HMX and RDX)

Stable EM

- Tested thermal stability up to 300°C
- Satisfying ageing tests

Green EM

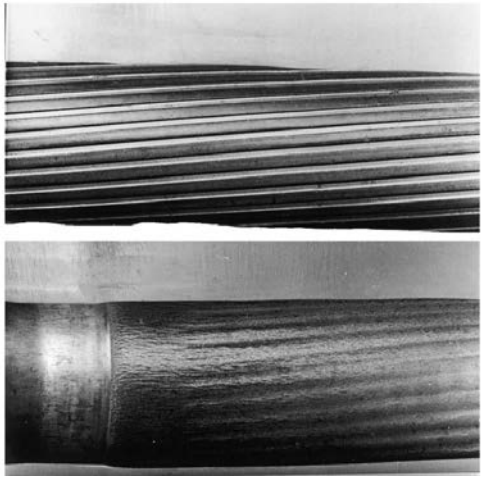
- REACH compliant
- Decreased toxicity
- Clean combustion products (mainly N_2)

Introduction

- **Why azole-based salts are suitable candidates ?**

Cold EM

- Low flame temperature
- Decreases erosivity in the gun barrel



Lawton, B. "Thermo-chemical erosion in gun barrels" *Wear* 251.1-12 **(2001)**: 827-838.

$$(\Delta m/m_c)_{max} = const. \cdot (\kappa M T_f)^4$$

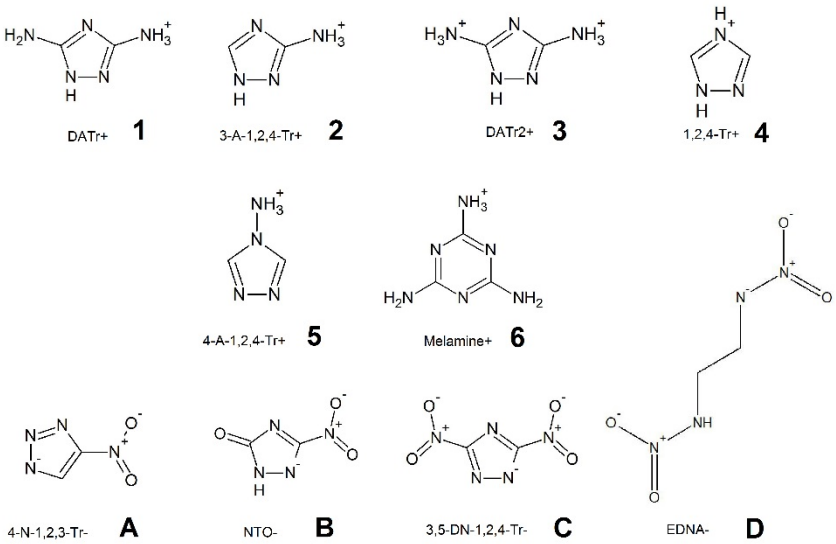
W. Kegler, D. Grune - **ISL**, Bericht 6 / 68 (**1968)**

$$(\Delta m/m_c)_{max} = const. \cdot T_f{}^3$$

Langlotz, W. et al. “Method for the examination of the erosivity of gun propellants" *V13 – Proceedings of the Fraunhofer ICT Conference* **(2017).**

Introduction

- **Strong synthesis and formulation knowledge**
- **Many possible anion/cation combinations**
- **Tests for all combinations are expensive (time and money)**



- **Heat of combustion (ΔH_c or Q_{comb}) measured with bomb calorimeter for 10 triazole-based salts**

$$C_aH_bO_cN_d + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) \rightarrow aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g)$$

$$\Delta H_c = -Q_{comb} = a\Delta_f H^0_{CO2(g)} + \frac{b}{2}\Delta_f H^0_{H2O(l)} - \Delta_f H^0_{Salt}$$

Introduction

$$\Delta H_c = -Q_{comb} = a\Delta_f H^0_{CO2(g)} + \frac{b}{2}\Delta_f H^0_{H2O(l)} - \Delta_f H^0_{Salt}$$

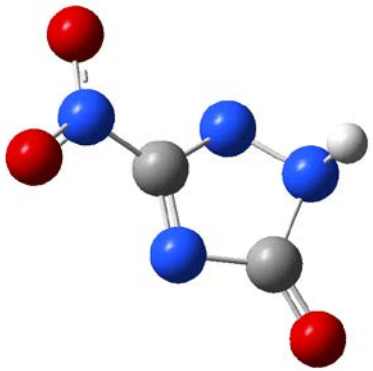
- **Heat of formation, the key property:**
  - Enable to estimate properties of interest such as force constant, detonation velocity, detonation pressure and sensitivities
  - Can be calculated thank to quantum chemical calculations

Objective: Validate a computational method to able to screen materials before their synthesis

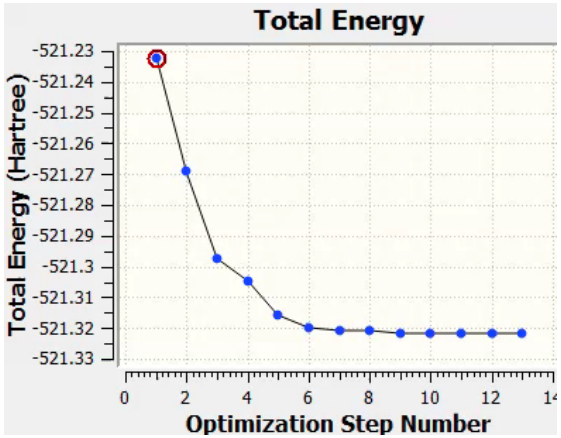
Theoretical approach

Expanding the limits of computational chemistry

- Calculations performed with Gaussian 16 software package
- Positive (or negative) charge is taken into account – Standard conditions



Molecule design (Gaussview)

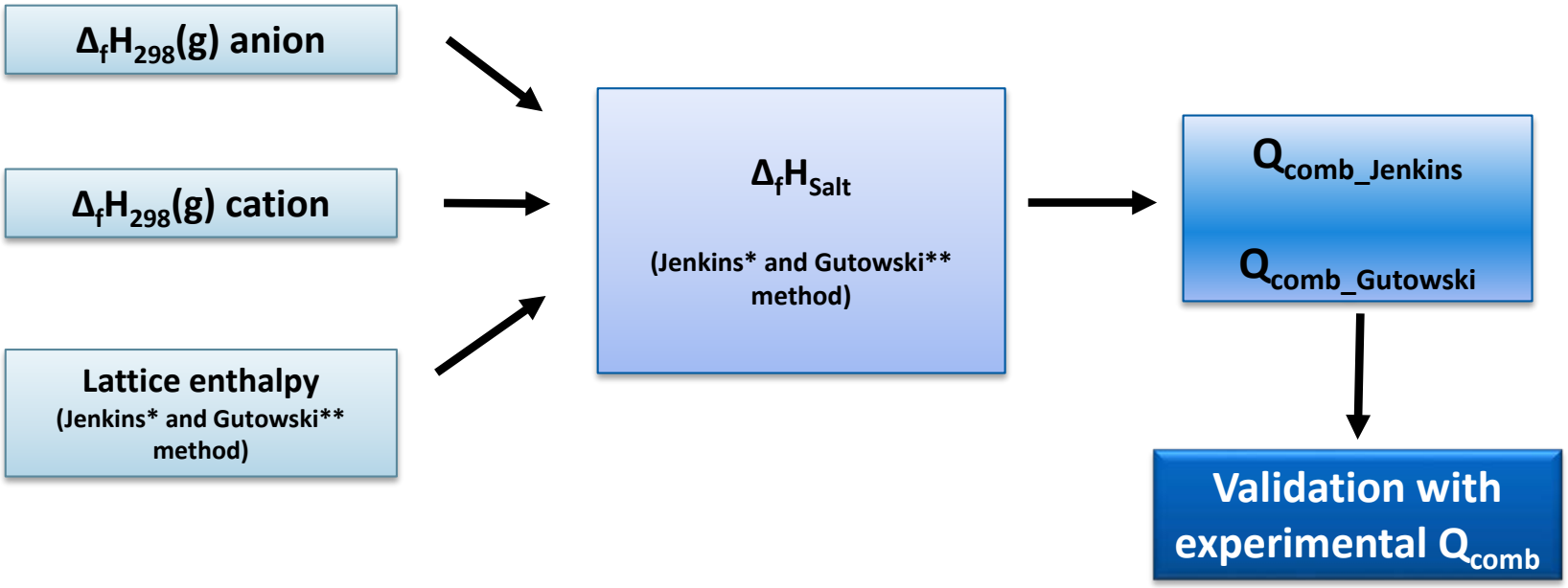


Optimization Calculation (Gaussian)

- Geometry optimization
- Energy calculation and molecular volume

Theoretical approach

- **Calculation pattern:**

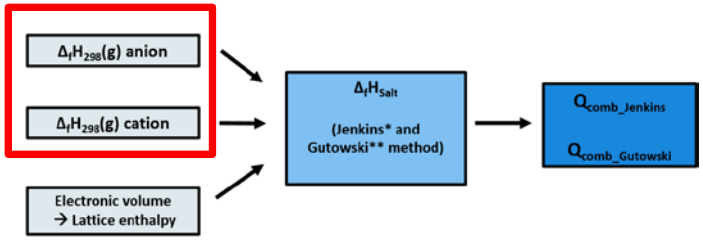


* H. Donald Brooke Jenkins, David Tudela et Leslie Glasser. « Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements ». Dans : *Inorganic Chemistry* 41.9 (2002), p. 2364–2367.

** Keith E. Gutowski, Robin D. Rogers et David A. Dixon. « Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations ». Dans : *The Journal of Physical Chemistry B* 111.18 (2007), p. 4788–4800.

Theoretical approach

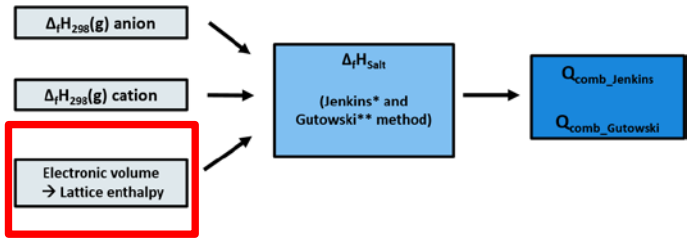
- **$\Delta_f H_{anion}$ and $\Delta_f H_{cation}$ (standard conditions)**



- **4 levels of theory investigated**
  - B3LYP 6-31G (d,p) with atomic corrections (***Osmont et al.*** *– Combust. Flame, vol. 151,* ***2007***)
  - CBS-4M (***Klapötke et al.*** *– Z. Anorg. Allg. Chem., 1309-1313,* ***2011***)
  - CBS-QB3 (***Forquet et al.*** – Chem. Asian j. 11, 730.44, ***2016***)
  - G4 **(proposed method)**

Theoretical approach

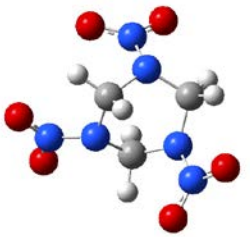
- **Lattice enthalpy ΔH_L**



  - Electronic volume calculation (B3LYP 6-31G (d,p) level)

$$V(\mathrm{M}_p\mathrm{X}_q) \approx pV(\mathrm{M}^{q+}) + qV(\mathrm{X}^{p-})$$

  - Calculation of the Lattice energy ΔU_L – **α** and **β** are constant values taken from Jenkins *et al.** or Gutowski *et al.***



$$\Delta U_L(\mathrm{M}_p\mathrm{X}_q,\,\mathrm{s}) = 2I\left(\frac{\alpha}{\sqrt[3]{V}} + \beta\right) = \left(pq^2 + qp^2\right)\left(\frac{\alpha}{\sqrt[3]{V}} + \beta\right)$$

  - Calculation of the Lattice enthalpy ΔH_L

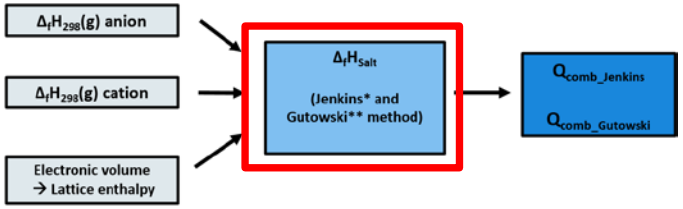
$$\Delta H_L(\mathrm{M}_p\mathrm{X}_q,\,\mathrm{s}) = \Delta U_L + \left(p\left(\frac{n_\mathrm{M}}{2} - 2\right) + q\left(\frac{n_\mathrm{X}}{2} - 2\right)\right)RT$$

* H. Donald Brooke Jenkins, David Tudela et Leslie Glasser. « Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements ». Dans : *Inorganic Chemistry* 41.9 (2002), p. 2364–2367.

** Keith E. Gutowski, Robin D. Rogers et David A. Dixon. « Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations ». Dans : *The Journal of Physical Chemistry B* 111.18 (2007), p. 4788–4800.

Theoretical approach

- $\Delta_f H_{salt}$

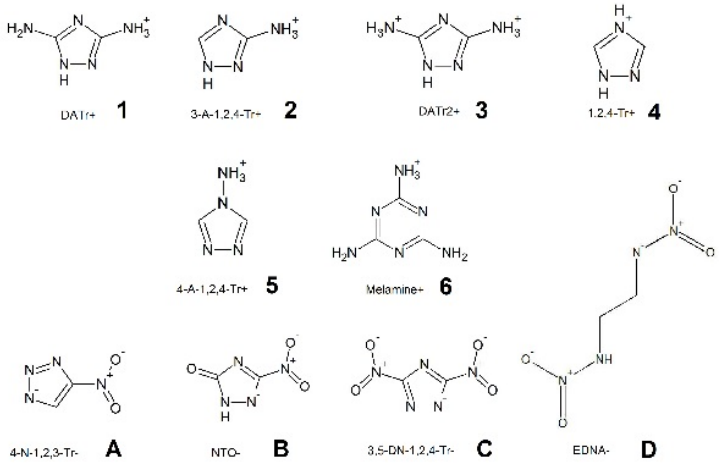


$$\Delta H_f(\mathrm{M}_p\mathrm{X}_q, \mathrm{s}) = p \times \Delta H_f(\mathrm{M}^{q+}, \mathrm{g}) + q \times \Delta H_f(\mathrm{X}^{p-}, \mathrm{g}) - \Delta H_L$$

- Q_{comb} ($C_aH_bO_cN_d$) is calculated and directly compared with experimental results

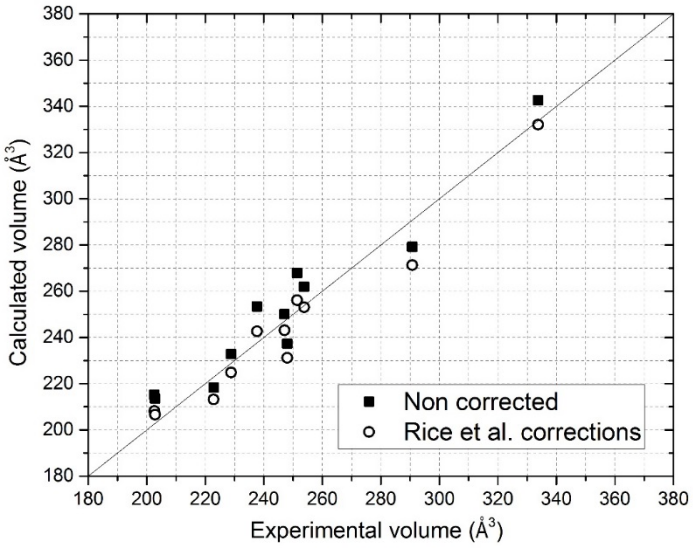
$$\boldsymbol{Q_{comb} = \Delta_f H^0_{Salt} - a\Delta_f H^0_{CO2(g)} - \frac{b}{2}\Delta_f H^0_{H2O(l)}}$$

Validation



- **Validation set with home made triazole-based salts**

- **Molecular volume validation**
  - Density measurements were conducted for each salts
  - Measured density is converted to volume (V=ρ/M). Predicted molecular volume are validated

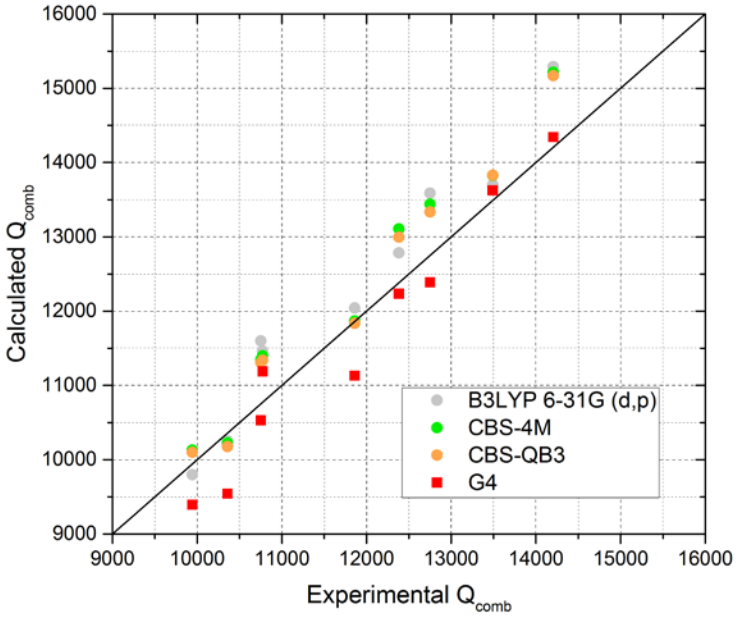


- **Mean errors:**
  - **Non corrected : 4 %**
  - **Rice et al. corrections : 2.8 %**

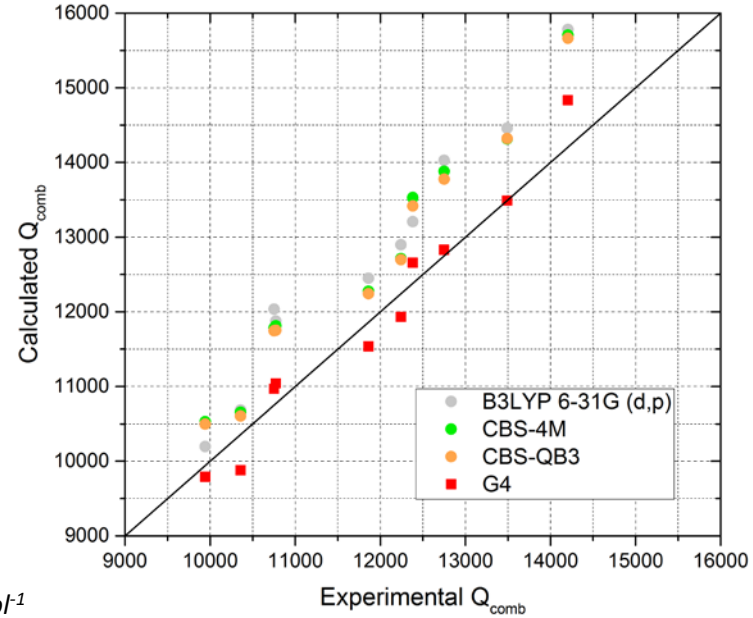
Rice B. M., Hare J. J. and Byrd E. F. "Accurate predictions of crystal densities using quantum mechanical molecular volumes" – *J. Phys. Chem. A* **(2007)**, 111, 10874.

Validation

- **Predicted Q_{comb} – Gutowski method**



- **Predicted Q_{comb} – Jenkins method**



Results in kJ.mol^{-1}

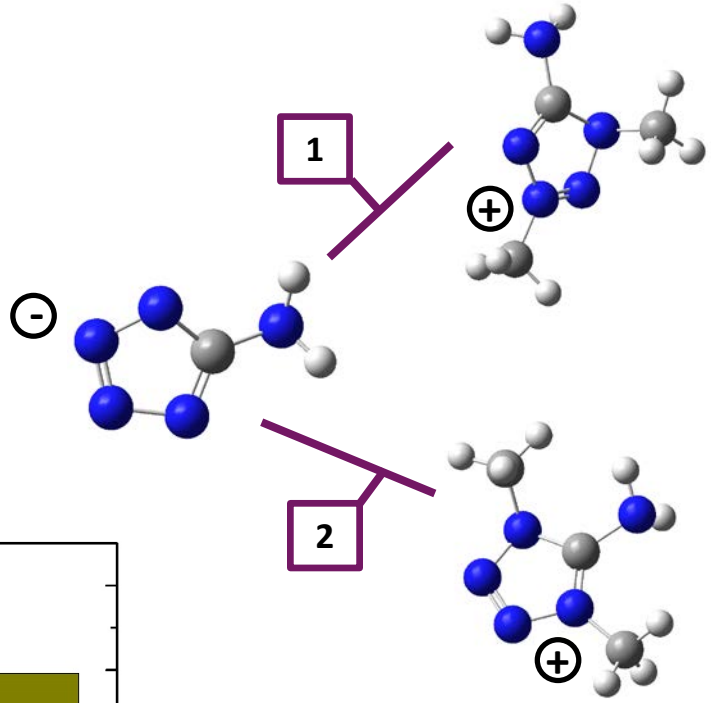
Mean Error (%)		
Level of theory	JENKINS	GUTOWSKI
B3LYP-6-31G(d,p)	7.3	4.1
CBS-4M	7	3.9
CBS-QB3	6.6	3.7
G4	2.3	3.5

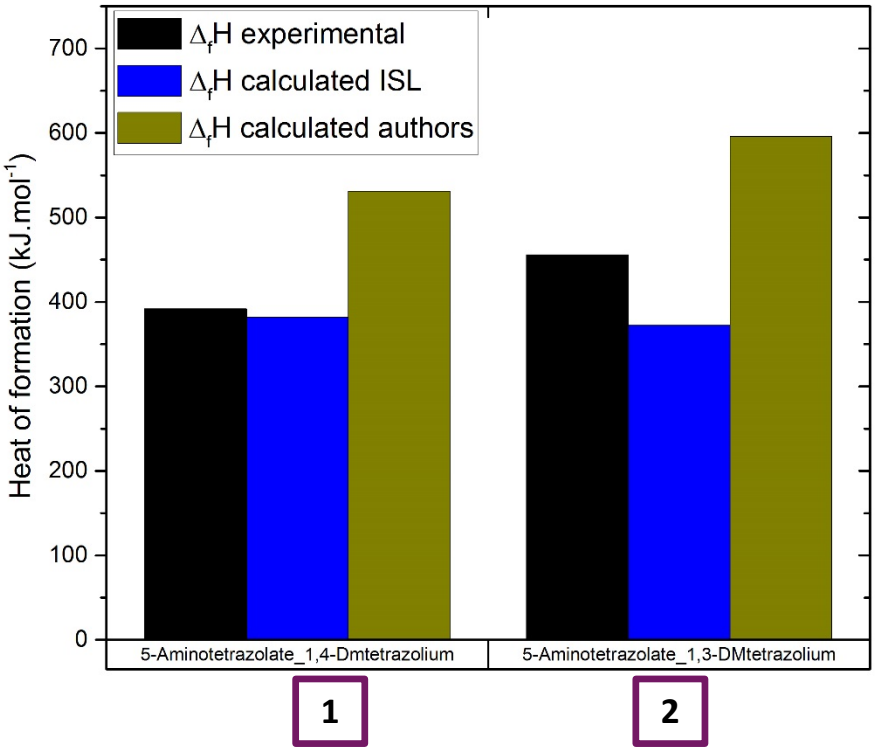
Method validated for triazole-based salts

Validation

- **Validation G4/Jenkins with other type of salts**

Klapötke, T. M., and Miró Sabaté C. *Zeitschrift für anorganische und allgemeine Chemie* 635.12 (2009): 1812-1822.

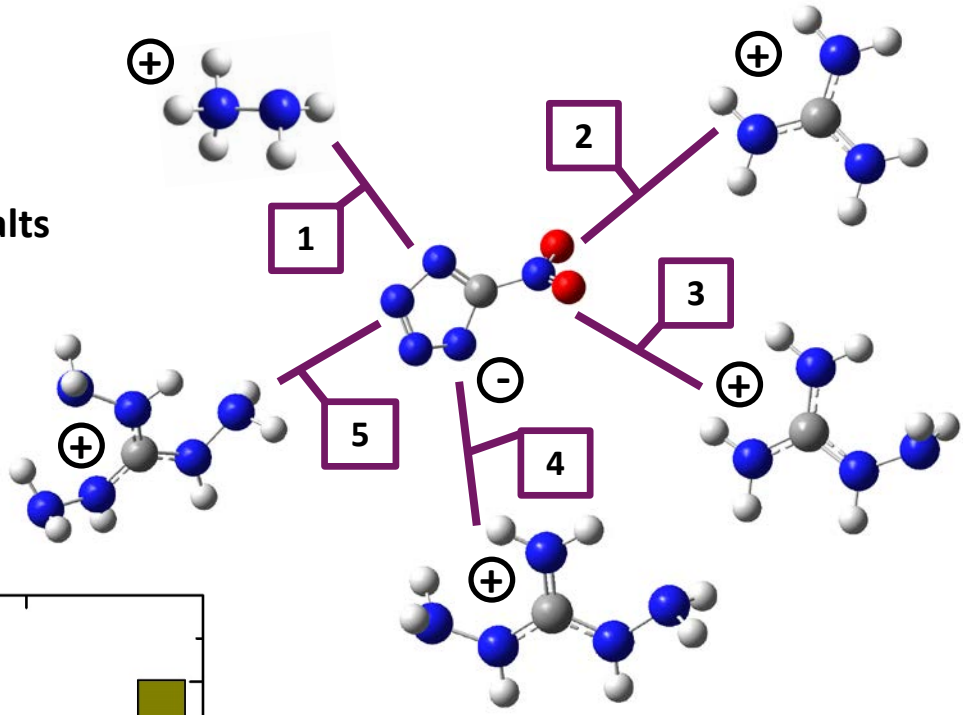


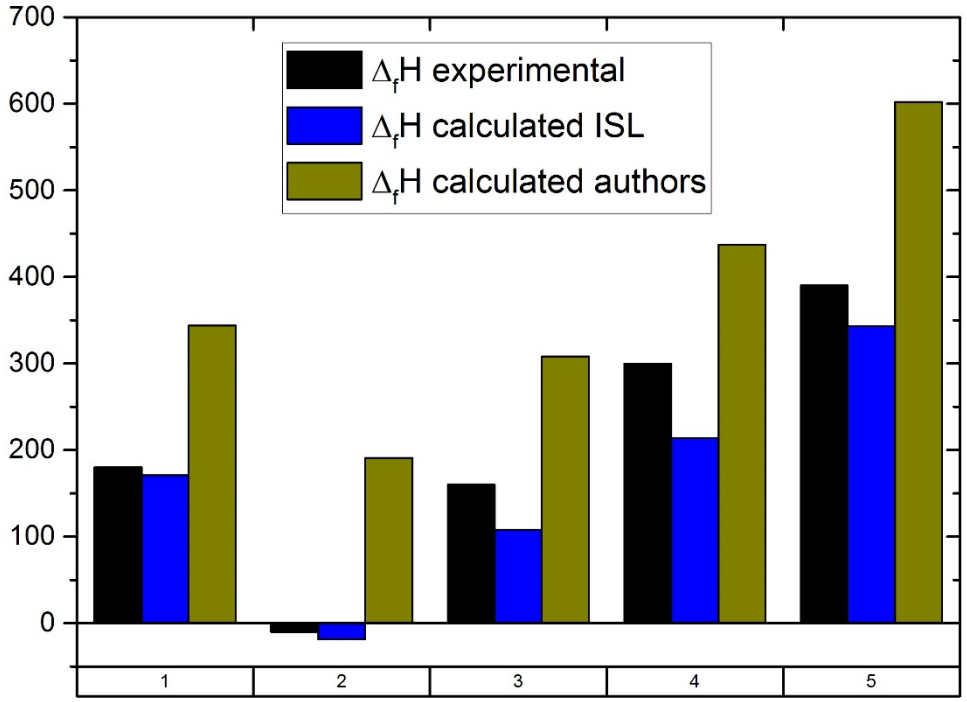


Validation

- **Validation G4/Jenkins with other type of salts**

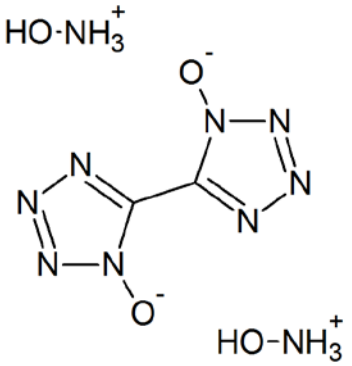
Klapötke, T. M., Mayer, P., Miró Sabaté, C., Welch, J. M., & Wiegand, N. (2008). *Inorganic chemistry*, *47*(13), 6014-6027.



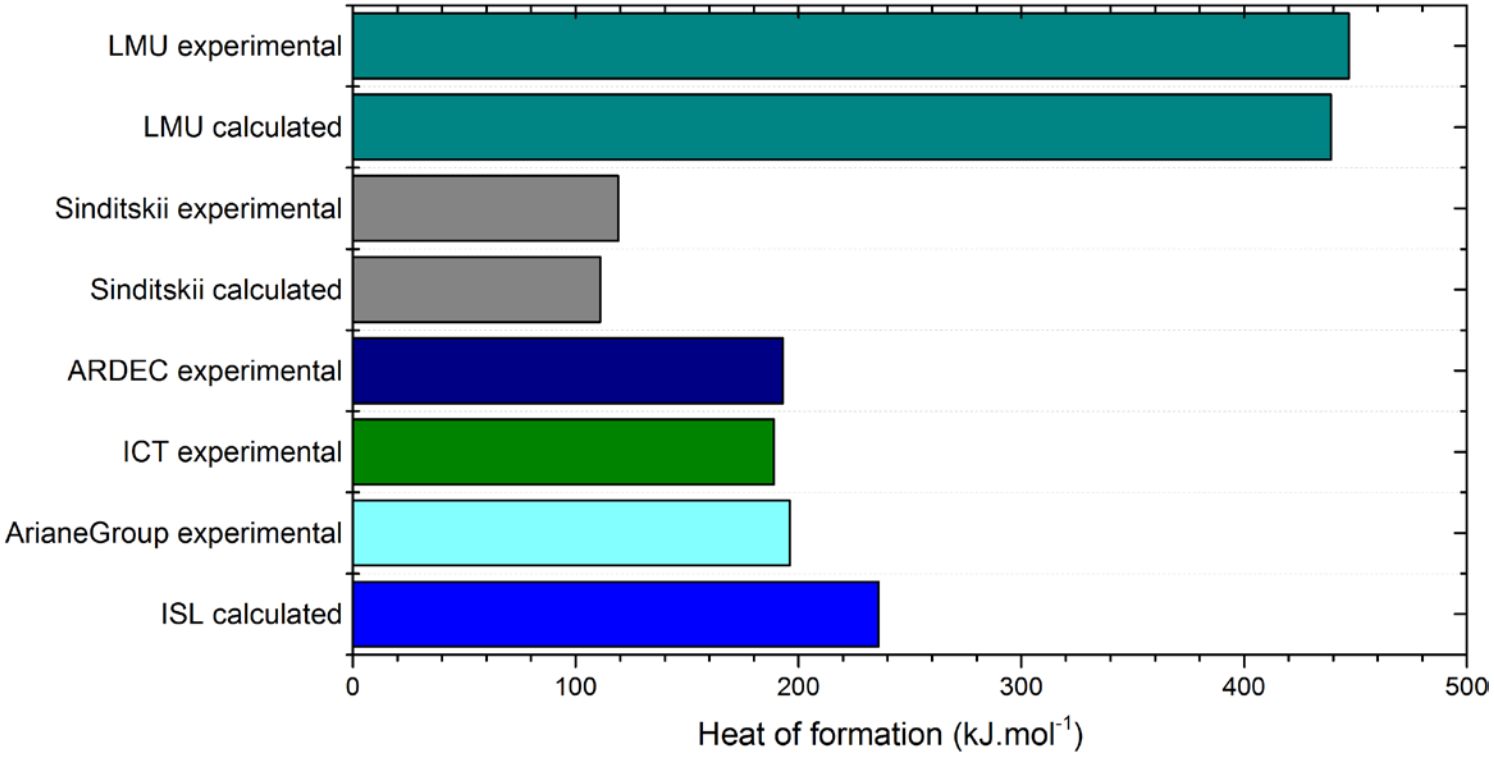


1. Hydrazinium 5-Nitrotetrazolate
2. Guanidinium 5-Nitrotetrazolate
3. Aminoguanidinium 5-Nitrotetrazolate
4. Diaminoguanidinium 5-Nitrotetrazolate
5. Triaminoguanidinium 5-Nitrotetrazolate

Validation



- **Validation with a commercial salt: TKX-50**
  - Synthesized at Ludwig-Maximilians-universität Munich (Fischer, N., Fischer, D., **Klapötke, T. M.**, Piercey, D. G., & Stierstorfer, J. (2012). *Journal of Materials Chemistry*, *22*(38), 20418-20422).



Data Courtesy of Dr. Thomas Keicher – Fraunhofer ICT

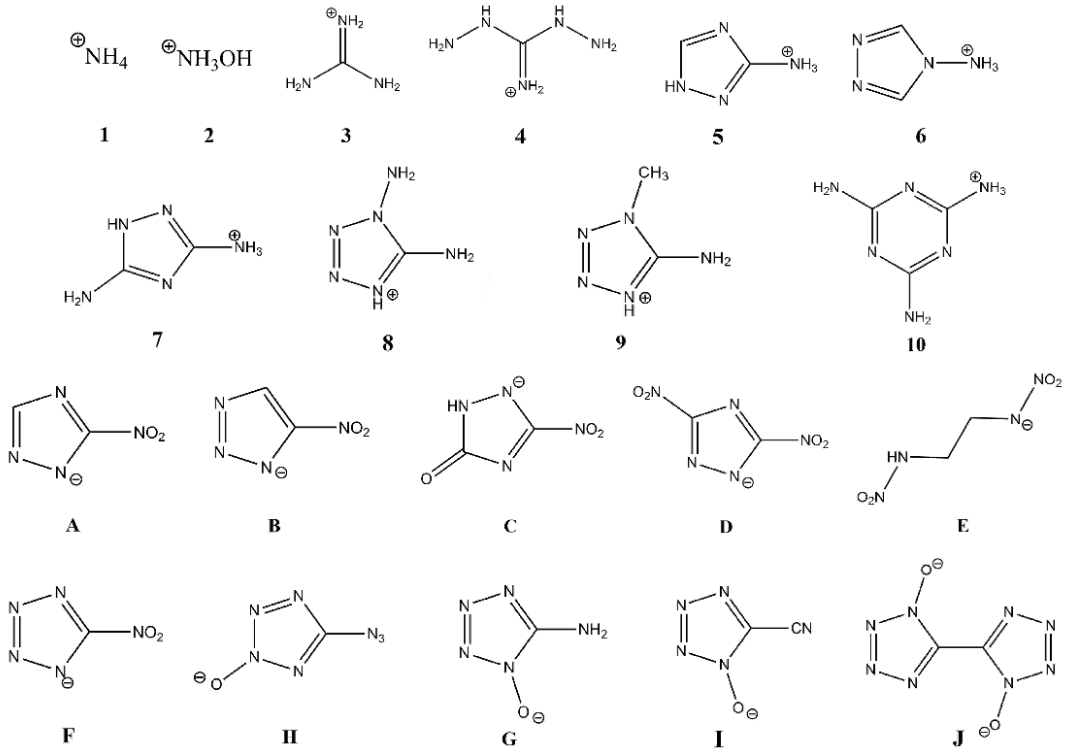
Results

- **Force vs flame temperature: a computational study**

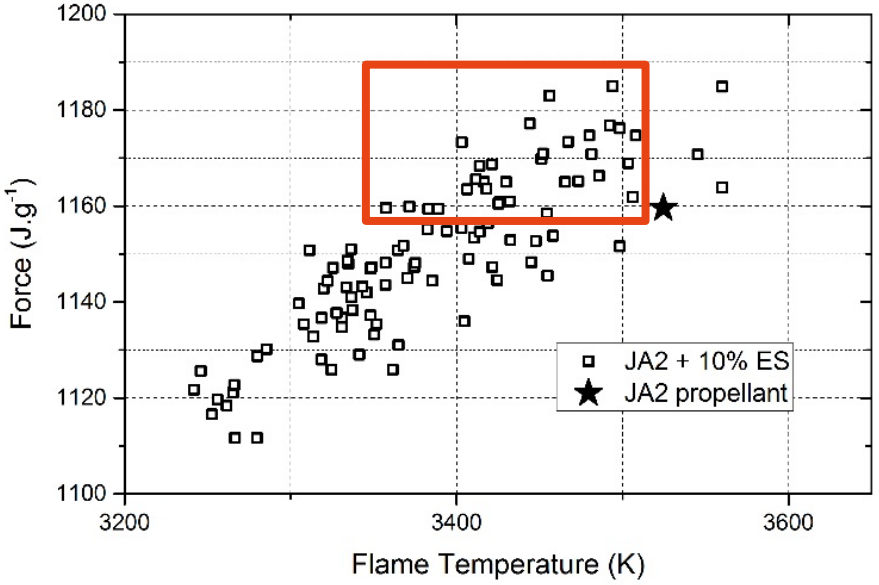
  - ICT code calculations using calculated properties : **heat of formation** and **density**

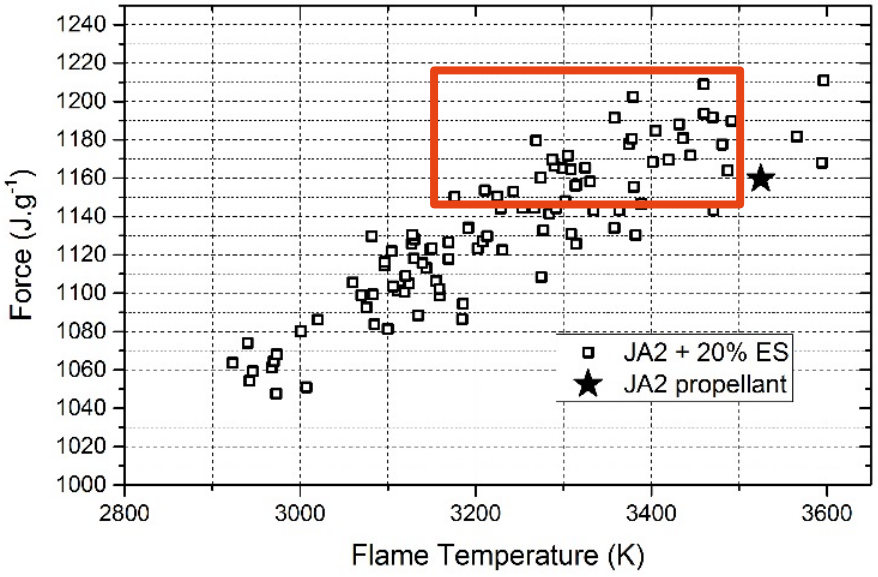
  - Comparison between **commercial propellant** (JA2) and "**commercial-like**" propellant (same composition but includes **10**, **20** or **30**% of energetic salt)

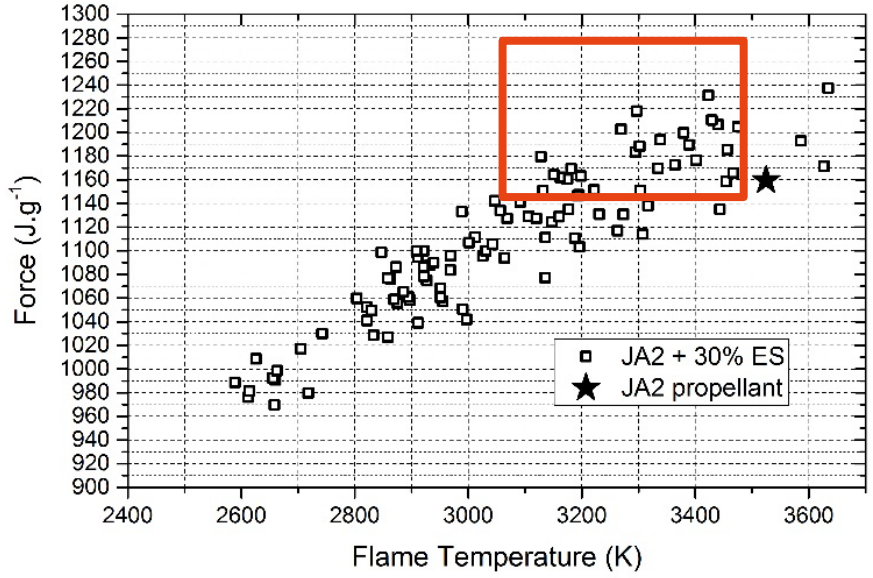
  - **100 potential azole-based salts** investigated



Results







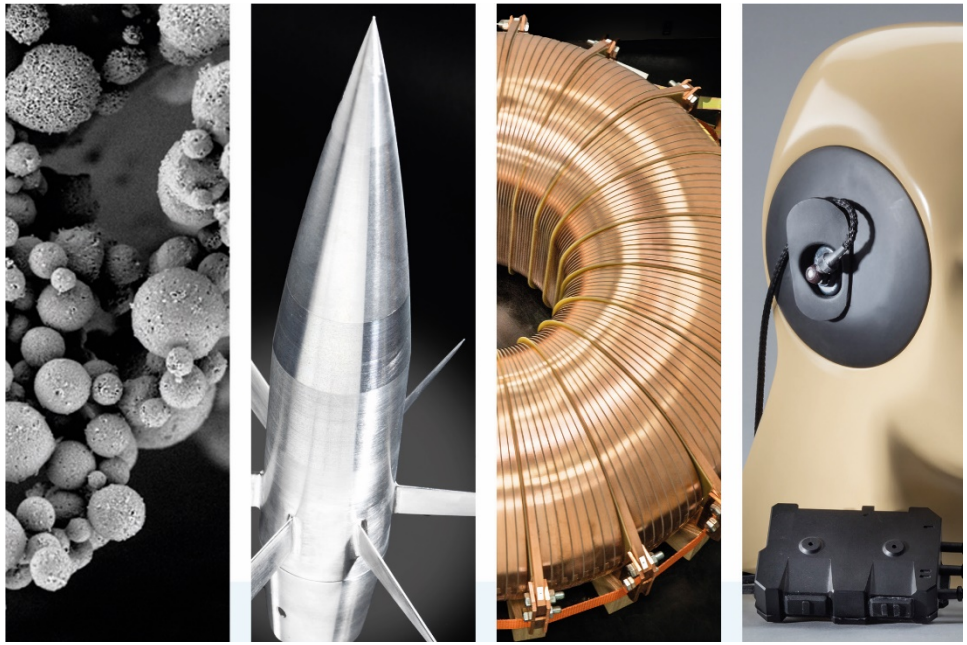
- **Comparison between JA2(★) and "commercial-like" propellant (□)**
- **Potential salts are in red square**

Conclusion

- **Computational method to predict heat of formation validated for triazole-based, tetrazole-based and guanidinium-based salts**

- **Ballistic performances of gun propellant containing azole-based salts**

- **Methodology to select anion/cation pairs with low flame temperature and enhanced force**



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60 YEARS