Plasma–assisted conversion of methane and carbon dioxide: Improving the energy efficiency

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1. Background
   - Exploring CH_4 and CO_2 for future energy sources
   - An opportunity for plasma systems?
2. Conversion of CH_4 in a DBD
   - Experimental results with $CH_4/CO_2/He$ mixtures
   - Electron kinetics in $CH_4/CO_2/He$ mixtures
   - A model for breakdown
   - A model for CH_4 and CO_2 conversion
3. Application of over-voltages
4. Future work
   - Perspectives

Chemical conversion of methane

- CH_4 + oxidant (O_2, CO_2, H_2O) → H_2 + CO (Syngas)
    - Syngas → H_2
    - Syngas ⇒ Fisher-Tropsch ⇒ synthetic fuels
- CH_4 + oxidant ⇒ CH_3OH (methanol)

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Perspectives

- *Conversion of natural gas into liquid fuels → large-scale plants;*
- *Hydrogen for fuel cells → compact and small syngas units.*

Atmospheric pressure plasmas

Dielectric barrier discharge

http://www.pages.drexel.edu/~rpg32/Research.htm

Gliding arc

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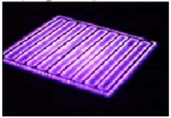

Surface discharge

- **Non-thermal process (room temp)**
- **Throughput necessary (scale !)**
- **Scalable (stacked microreactors?)**
- **Essentially nonequilibrium**
- **Controle of EEDF**

DBD/Packed bed
Catalytic reaction enhanced by *Plasma catalysis*.

Corona discharge

http://www.jeh-center.org/electro/plasma/theory.html

Non-thermal plasmas for conversion of CH_4

Main plasma sources used in the conversion of CH_4:

- Dielectric Barrier Discharges
  1. Atmospheric pressure (normally in the filamentary mode);
  2. High electron density and energy;
  3. Easy to scale up;
  4. Coupling between the plasma and a catalyst facilitated.
  5. But. . . works at low gas flux
  6. But. . . low electrode spacing
  7. But . . . until now, low energy efficiency
- Gliding arc: $T_e = 1 - 3\,eV \gg T_g \sim 2000\,K$ and $T_v \sim 2T_g$.
- Microwave discharges

How to increase the energy efficiency?

Options:

1. Dilution with rare gases ▸ cs;

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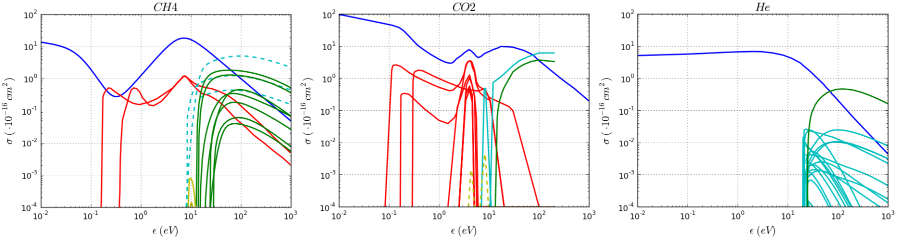
1. Dilution with rare gases ▸ cs;
2. Use of over-voltages ▸ VI;

e-collision cross sections



Legend:

— momentum transfer; — vibrational excitation; — electronic excitation;
— ionisation; — attachment.

Definitions

Some definitions:

- Conversion of a reactant X: $C_X = \frac{[X]_0 - \alpha[X]}{[X]_0}$
- Selectivity for a product Y: $S_Y = \frac{\alpha n_Y [Y]}{\sum_X([X]_0 - [X])}$
- Specific input energy: $\mathcal{S} = P/q_V$
- Conversion ability (energy efficiency): $\eta_X = \frac{[X]_0 - \alpha[X]}{\mathcal{S}/c}$

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Conditions:

- AC power supply, (5–10) kHz, (room temperature);
- Electric diagnostics, GC;

N.Pinhão, A.Janeco and J.Branco *Plasma Chem. Plasma Process* (2011) 31:427-439

CH_4/CO_2/He mixtures: Breakdown voltage

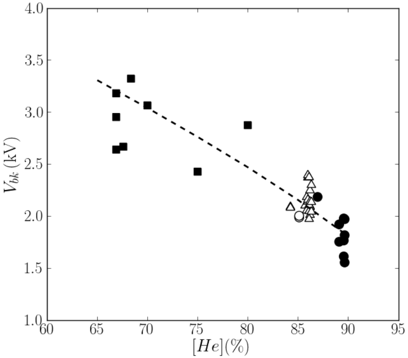


Figure : Gas breakdown voltage for CH_4/CO_2/He mixtures and $[CH_4]:[CO_2]=1$

$CH_4/CO_2/He$ mixtures: Conversion

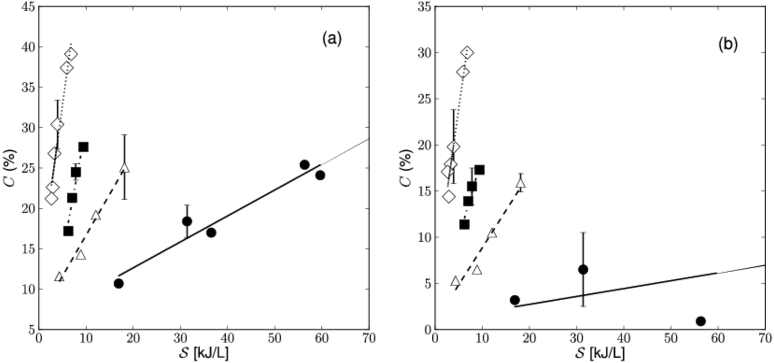
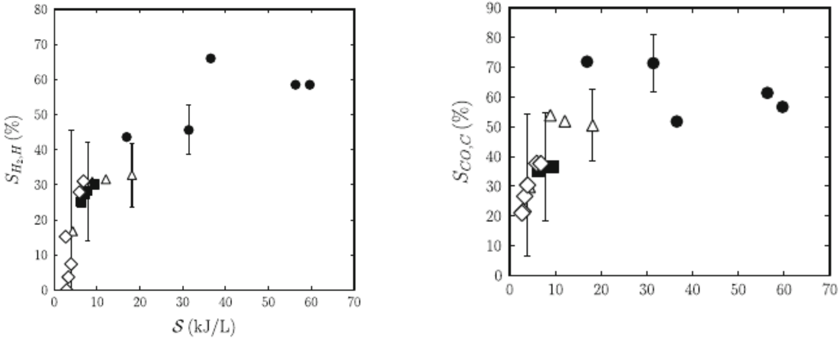


Figure : Conversion of (a) CH_4 and (b) CO_2 for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ($[CH_4]$:$[CO_2]$=1).

$CH_4/CO_2/He$ mixtures: Selectivity



Selectivity for H_2 and CO for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ($[CH_4]$:$[CO_2]$=1).

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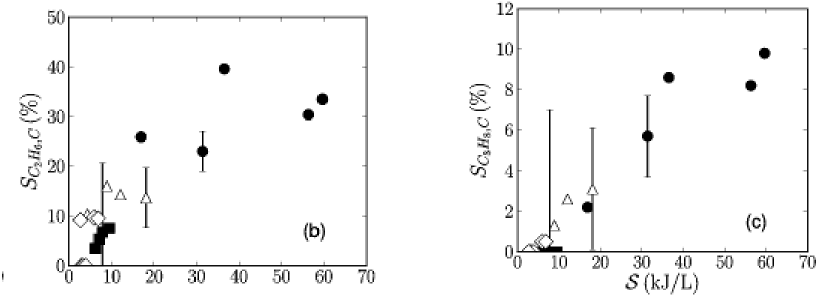

Selectivity for C_2H_6 and C_3H_8 for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ($[CH_4]:[CO_2]=1$).

CH_4/CO_2/rare gas mixtures: Summary

Table : Products and energy efficiency for CH_4 conversion in a DBD

Reference value[a] (H_2): 1.13 eV/molec.

Admixture		pure CH_4	+ O_2 or CO_2	+ He, Ar, Ne
Products		H_2, C_xH_y, solid-C	H_2, CO, CO_2[b], CH_3OH, $C_xO_yH_z$	
Conv. ab.	[total]	40	8.6	5.7
(MJ/mol)	[CH_4]	40	15	9
	[CO_2]	-	20	14
E. eff. (H_2)	eV/molec.	-	-	17
Comment		C-deposits	H_2O[b], liquid products	

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[a] Gutsol et al., *J. Phys. D: Appl. Phys.* **44** (2011) 274001

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Challenge:

How to explain the results?
How to increase the energy efficiency?

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Electron kinetics

Gas mixtures:

- Input: $\eta He/\frac{1}{2}(1-\eta)CH_4/\frac{1}{2}(1-\eta)CO_2$;

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- Boltzmann equation for an electron swarm: evdf depends on the electron density gradients;
- Hydrodynamic regime with non-conservative processes, multiterm;
- Results: f_0, α/N, $\nu_i/N = [M_i] \times k_e^X$, with $M_i = CH_4, CO_2, He$;

A.Janeco , N.Pinhão, and V.Guerra *Plasma Sources Sci. Techn.* (submitted)

a) Electron energy distribution function

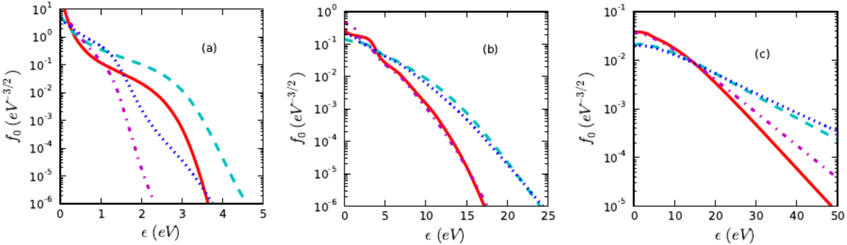

Figure : Isotropic component of the eedf for three values of reduced field, (a) 10 Td, (b) 74 Td and (c) 736 Td, and different combinations of (η, C): —— (0, 0); – – – (0.6, 0); — · — (0, 0.3); · · · · (0.6, 0.3).

b) Ionization coefficient

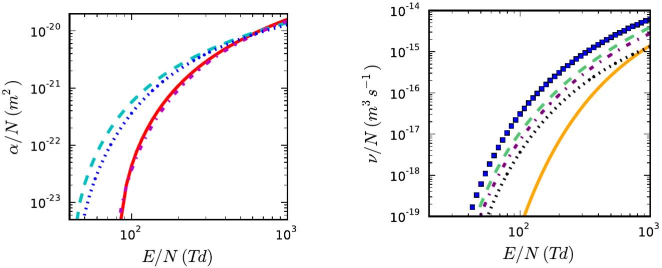

Figure : [left] Effective ionization coefficient as a function of the reduced field and for different values of (η, C): ——— (0, 0); – – – (0.6, 0); — · — (0, 0.3); · · · · (0.6, 0.3). [right] Ionization reduced frequencies for ——— He, ☐ CH_4, — — — CO_2, — · — CO and · · · · H_2 as a function of the reduced field for a (η, C) = (0.6, 0.3).

c) Vibrational excitation frequencies

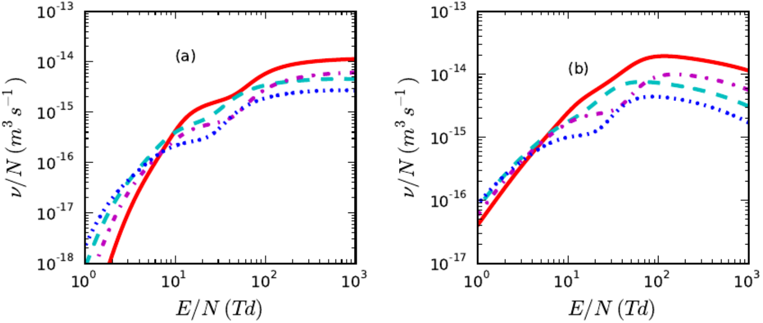

Figure : Total vibrational reduced collision frequencies in (a) CH_4 and (b) CO_2 as a function of the reduced field and for different values of (η, C): [same codes as before].

d) Ionization and excitation of He metastable levels

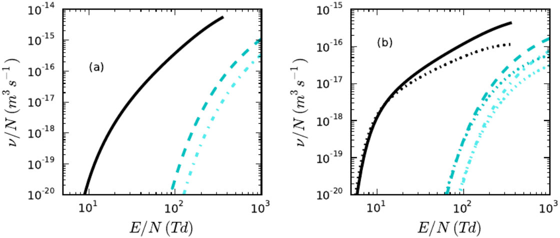

Figure : (a) Electron collision reduced frequencies for helium ionization and (b) excitation of helium metastables as a function of the reduced field and for different values of (η, C). Ionization or 2 ^{1}S: —— (1, 0); – – – (0.6, 0); — · — (0.4, 0). For 2 ^{3}S: dotted curves (· · ·) with the same colors as before.

e) Fractional energy losses

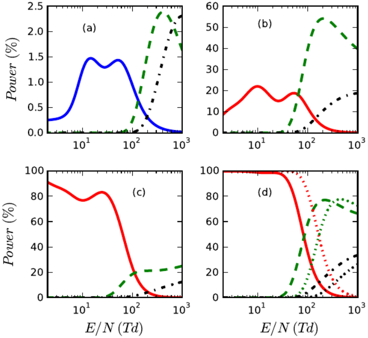

Figure : Fractional power losses for each type of process and mixtures component: (a) He, (b) CH_4, (c) CO_2 and, (d) the whole mixture. —— momentum transfer; —— vibrational exc.; − − − electronic exc.; — · — ionization. Calculations made for $(\eta, C) = (0.6, 0)$, with the exception of the dotted curves $(\cdot\cdot\cdot\cdot)$ in (d), corresponding to $(\eta, C) = (0, 0)$.

Summary

Role of helium:

- Significant shift of the evdf to higher energy;
- Responsible for an increase of the electronic exct. and ionization frequencies in CH_4 and CO_2;
- Responsible for a shift of the α/N curve to lower E/N values;
- The excitation and ionization frequencies in He are negligible;
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Effect of conversion:

- Depends on process and E/N range;
- Process with ε_o low, increase at low E/N and decrease afterwards;
- Process with ε_o high are relatively insensitive and $\nu \propto [M]$;

Breakdown voltage

Model: Townsend regime

1. Discharge starts as a Townsend avalanche;
2. Electric field undisturbed: $E(r) \propto U_{bk,g}/r$;
3. $1/\nu_{inel} < 0.1\,ns \Rightarrow f_e\left(\mathbf{r}, \mathbf{v}, t\right)$ in local field equilibrium;
4. Initial development sustained by photo-electric effect;
5. Breakdown criteria: $\int_{r_o}^{R} \alpha_{eff}(E(r)/N)dr = \log(1+\gamma^{-1})$

Breakdown voltage

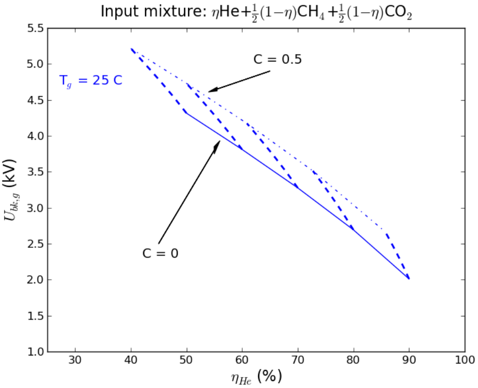
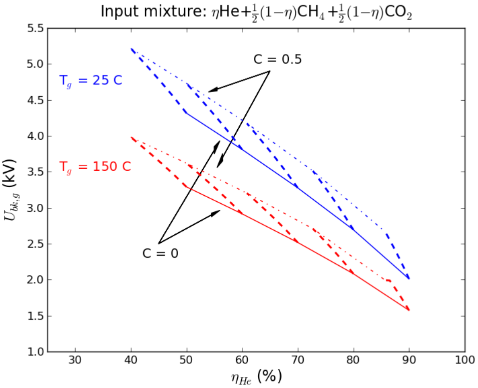


Figure : Gas breakdown voltage for CH_4/CO_2/He mixtures and $[CH_4]:[CO_2]=1$. Experimental (points) and model (lines) results.

Breakdown voltage



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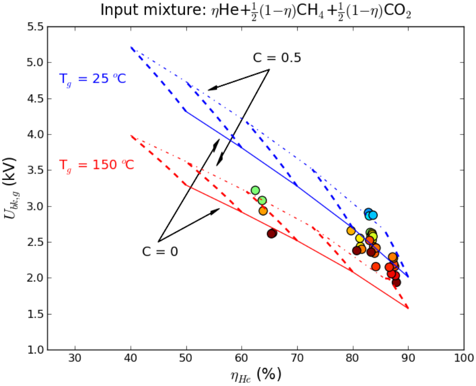

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CH_4 and CO_2 conversion

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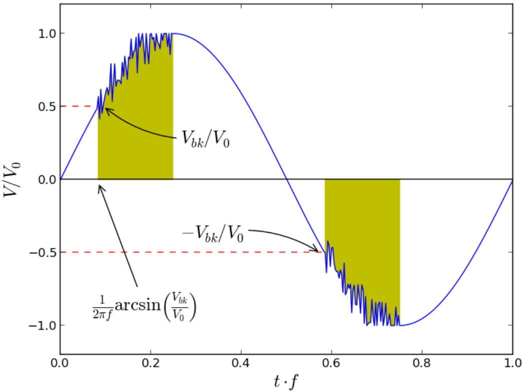
4. Time average model in T: $f_T(U_{bk}/U_{max,e})$.


V/V_0
1.0
0.5
0.0
−0.5
−1.0
0.0
0.2
0.4
0.6
0.8
1.0
$t \cdot f$
V_{bk}/V_0
$-V_{bk}/V_0$
$\frac{1}{2\pi f}\arcsin\left(\frac{V_{bk}}{V_0}\right)$

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2. $l_{equiv} \sim \overline{v_d}\, \delta t_{microdisc}$.
3. $\overline{\alpha} \Rightarrow \overline{E/N} \Rightarrow \overline{K_e^*} \Rightarrow 60\,Td < \overline{E/N} < 90\,Td$;

Model equations and species

Products involved in conversion:

CH_4: CH_3, CH_2, CH, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+, H^-, CH_2^-;
CO_2: $O(^1S)$, O^+, CO^+, C^+, O^-

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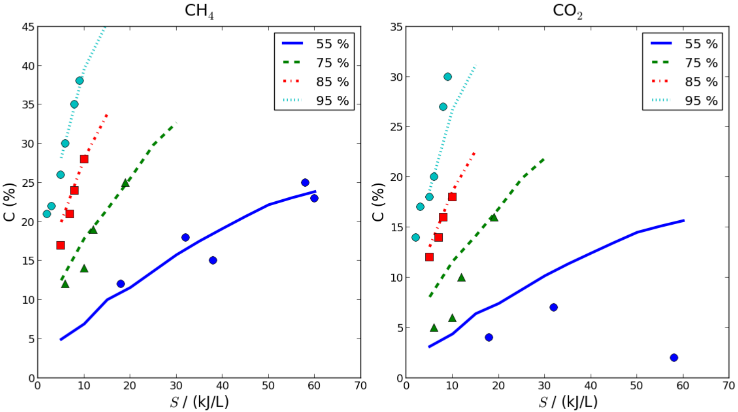
CO_2: $O(^1S)$, O^+, CO^+, C^+, O^-
He: $He(2^3S)$, $He(2^1S)$

In steady state:

$$\frac{d\rho v_{gas}}{dz} = 0$$

$$\frac{d}{dz}\left[n^i(z)(v_{gas}+V_D)\right] = -f_T f_V \frac{Q_{gas}}{q_e} c^i(z) \sum_j \frac{\overline{K_e^{ij}}(z)}{\overline{\alpha}(z)/N\xi} - K_P^i n^i(z) n_{He*}(z)\,, \qquad i = CH_4, CO_2$$

Model results



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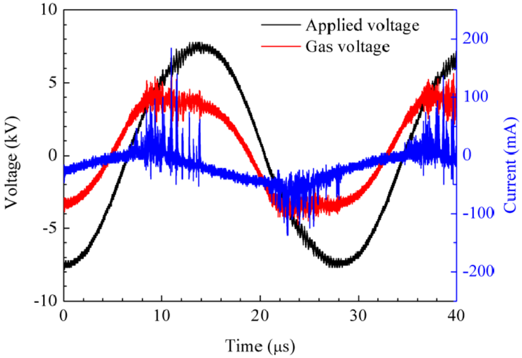
V-I


Applied voltage
Gas voltage
Voltage (kV)
10
5
0
-5
-10
Current (mA)
200
100
0
-100
-200
0
10
20
30
40
Time (μs)

Results with a rectangular power supply

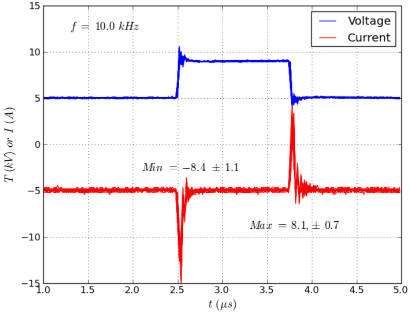


Figure : Voltage and current signals with a rectangular power supply on mixtures of CH_4/CO_2 with 60% He.

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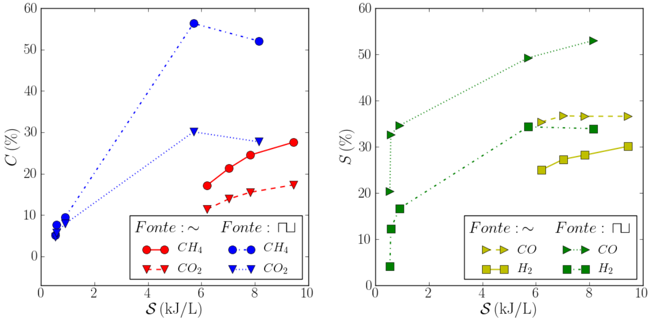

Figure : Conversion and selectivity results obtained with sinusoidal or rectangular power supplies on mixtures of CH_4/CO_2 with 80% He. Conversion ability: (5.7 → 1.8) MJ/mol (H_2 : 6 $eV/molec.$)

CH_4/CO_2/rare gas mixtures: Summary

Table : Products and energy efficiency for CH_4 conversion in a DBD
Reference value (H_2): 1.13 eV/molec.

Admixture		$CH_4 + CO_2 + He$
Sinusoidal power supply kHz):		
Cv. ab.	[total]	5.7
(MJ/mol)	[CH_4]	9
	[CO_2]	14
$E_{eff}(H_2)$	eV/molec.	17
Pulsed power supply:		
Cv. Ab.	[total]	1.8
$E_{eff}(H_2)$	eV/molec.	6

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- Long term goal: model for V-V and V-T kinetics

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We need cross sections!

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- Explain the results with pulsed power.

Good Vibrations!

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- Extend V-V and V-T theory to polyatomic molecules.