Laboratory Investigation of Key Astrochemical Reactions Involving Nuclear Spin Isomers of Dihydrogen or Trihydrogen Cations

M. Hejduk

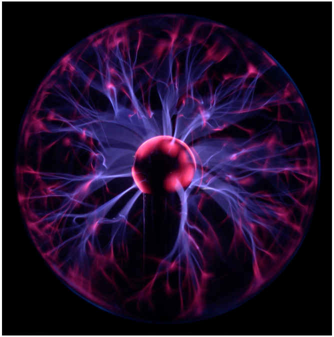
P. Dohnal, P. Rubovič, I. Zymak, D. Mulin, P. Jusko, Š. Roučka, Á. Kálosi,
R. Plašil, D. Gerlich, J. Glosík
Bernd von Issendorff

Faculty of Mathematics and Physics
Charles University in Prague
Albert-Ludwigs-Universität Freiburg

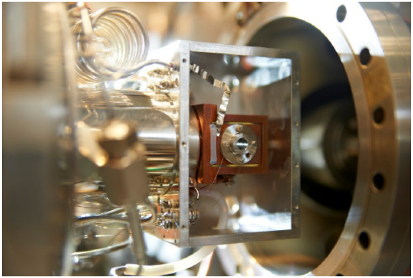
Contents

Overview

Plasma lamp, Wikipedia



22PT apparatus, Zymak I., Thesis, 2013



H_3^+-e^- recombination

$H_3^+ + e^- \rightarrow 3H, H_2 + H$

Ion-molecule reactions

- $N^+ + H_2 \rightarrow NH^+ + H$
- $H^+ + H_2 \rightarrow H_3^+ + h\nu$

- Everything at temperatures below 120 K.
- Everything with regard to nuclear spin states (NSS).

Motivation

In interstellar medium:

- $H_3^+ \xrightarrow{O} OH^+ \xrightarrow{H_2} H_2O^+ \xrightarrow{H_2} H_3O^+ \xrightarrow{e} H_2O$
- $N^+ \xrightarrow{H_2} NH^+ \xrightarrow{H_2} \cdots \rightarrow NH_4^+ \xrightarrow{e} NH_3$

How H_3^+ ions are formed and destroyed, how the first element in ammonia formation chain proceeds?

Reactions are dependent on states:

Recombination processes

Rotational (nuclear spin) states of H_3^+

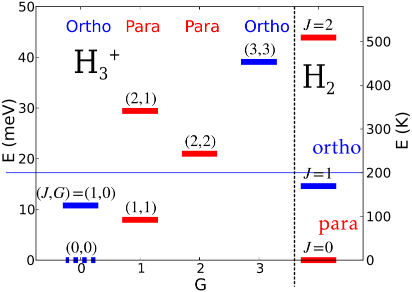
- $H_3^+(J,G) + e^- \rightarrow$ neutral products
- $H_3^+(J,G) + e^- + He \rightarrow$ neutral products + He

Ion-neutral reactions

Rotational (nuclear spin) states of H_2, fine-structure states of N^+

- $N^+(^3P_{j_a}) + H_2(j) \rightarrow NH^+ + H$
- $H^+ + H_2(j) \rightarrow H_3^+ + h\nu$
- $H^+ + 2H_2(j) \rightarrow H_3^+ + H_2$

Quantum mechanical structure of H_3^+ and H_2



Nuclear spin states (NSS) are coupled with specific rotational states.

No spontaneous interconversion!

Hidden energy (at low temperatures)!

Terminology

Para-H_2 ↑↓, abundance ${}^{\mathrm{p}}f_2$.

Ortho-H_2 ↑↑, abundance ${}^{\mathrm{o}}f_2$.

Normal-H_2 ${}^{\mathrm{p}}f_2 = 0.25$, ${}^{\mathrm{p}}f_2 + {}^{\mathrm{o}}f_2 = 1$.

Para-H_3^+ ↑↓↑, abundance ${}^{\mathrm{p}}f_3$.

Ortho-H_3^+ ↑↑↑, abundance ${}^{\mathrm{o}}f_3$.

Normal-H_3^+ ${}^{\mathrm{p}}f_3 = 0.5$, ${}^{\mathrm{p}}f_3 + {}^{\mathrm{o}}f_3 = 1$.

What we measure

We want to measure rate coefficients.

- Ex.: $A^+ + B \rightarrow C^+ + D$
- $\frac{d[A^+]}{dt} = -k \times [A^+][B]$
- Ex.: $A^+ + B + E \rightarrow C^+ + D$
- $\frac{d[A^+]}{dt} = -K \times [A^+][B][E]$ $\Rightarrow k = K[E]$
- $k = \langle \sigma v \rangle$

Rate coefficients depend on

kinetic (T_{Kin}), rotational (T_{Rot}), vibrational (T_{Vib}) temperatures and electronic excitation

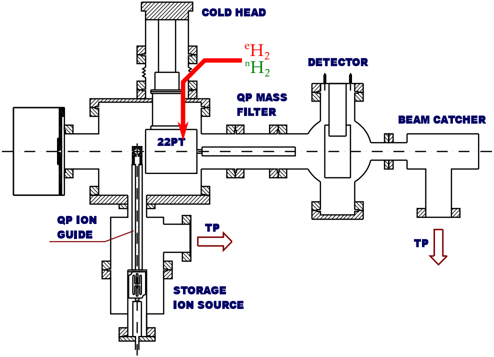
- $k = k(T_{Kin}, T_{Rot}, T_{Vib}, T_{el.} \dots)$
- $K = K(T_{Kin}, T_{Rot}, T_{Vib}, T_{el.} \dots)$

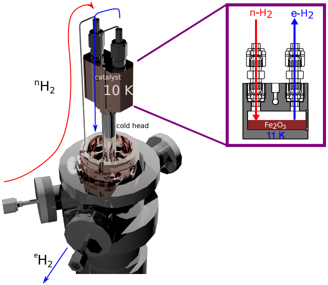
Compare with the state-dependency of the reactions.

We measure $[A^+](t)$ or $[C^+](t)$.

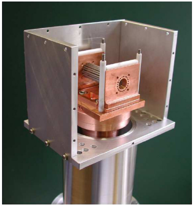
Studies of ion-molecule reactions by ion trap

22-pole RF trap



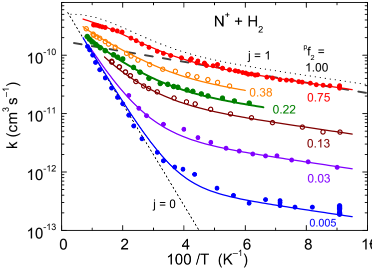


- Para-hydrogen generator attached
- $T_i = T_{Kin} = 10 - 300$ K, cooling by He buffer gas
- Number of ions ≈ 100 (because of detector)
- $P_0 < 10^{-7}$ Pa, $P_{exp} \approx 10^{-5} - 10^{-3}$ Pa
- MCP charge particle detector, mass analysis by QP mass filter



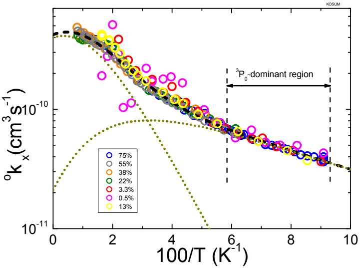
Dependence of $N^+ + H_2(j)$ reaction on $^3P_{j_a}$

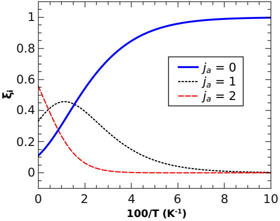
- Ortho-H_2 contributes to the reaction with higher energy (≈ 170 K) than para-H_2.



$(k - {}^{p}k^{p}f_2)/{}^{o}f_2$

$$k = {}^{o}k^{o}f_2 + {}^{p}k^{p}f_2$$





Temperature dependence is not purely Arrhenius type! Thermalization of FS states!?

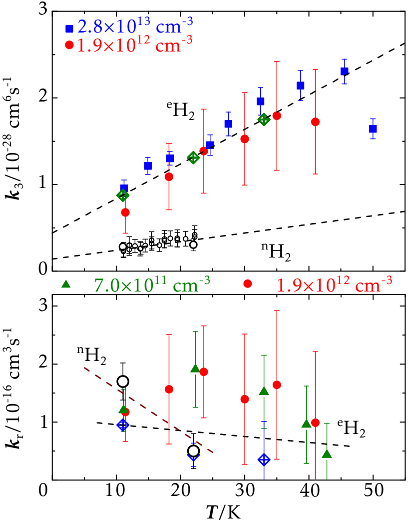
$H^+ + H_2$ association

Two channels

- $$H^+ + \begin{cases} {}^{p}H_2 & \xrightarrow{{}^{p}k_{rad}} \\ {}^{o}H_2 & \xrightarrow{{}^{o}k_{rad}} \end{cases} H_3^+ + h\nu$$
- $$H^+ + \left\{ \begin{matrix} {}^{p}H_2 \\ {}^{o}H_2 \end{matrix} \right\} + \begin{cases} {}^{p}H_2 & \xrightarrow{{}^{p}k_3} \\ {}^{o}H_2 & \xrightarrow{{}^{o}k_3} \end{cases} H_3^+ + H_2$$

Coefficients k_{rad} a k_3 were never measured at $T < 80$ K with regards to NSS distribution of H_2.

$H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2$: TEMPERATURE DEPENDENCE



$$k_{\text{eff}} = k_{\text{rad}} + k_3[H_2]$$

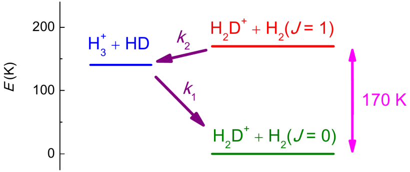
Questions

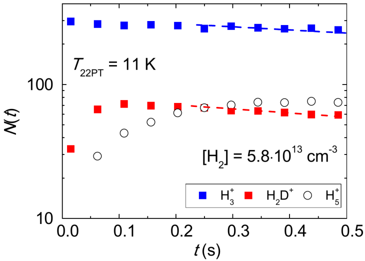
- Why $k_3 \propto T$?
- Transition state theory: $k_{\text{rad}} \propto \tau_{\text{dis}}(H_3^{+*}) \propto T^{-1.9}$: why it is not kept for $^eH_2$?

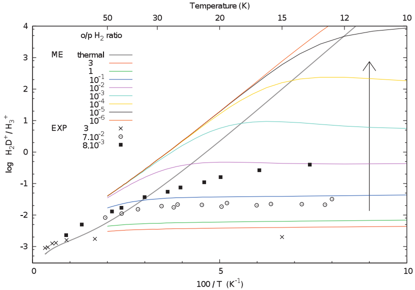
D. Gerlich and S. Horning, *Chemical Reviews*, **92**(7):1509–1539, 1992.

Influence of hydrogen deuteride impurities

$$H_3^+ + HD \leftrightarrows H_2D^+ + H_2 + \Delta E$$







Terrestrial abundance
$[HD]/[H_2] = 3.2 \times 10^{-4}$

Steady state ratio $[H_2D^+]/[H_3^+] = 0.2 \Rightarrow {}^{p}f_2 \approx 0.01$

Hugo E., Asvany O., Schlemmer S., J. Chem. Phys. 130, 164302, 2009

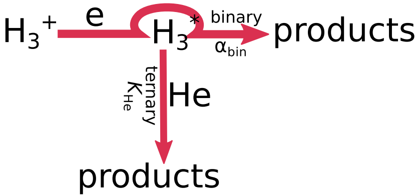
Plasma experiments: H_3^+-e^- recombination

H_3^+-e^- recombination in afterglow

- $[H_3^+] = n_e$
- rate equation: $\frac{dn_e}{dt} = -\alpha_{eff} n_e^2 - \nu n_e$

Binary and ternary rec.

Pressure ~ 1 mbar



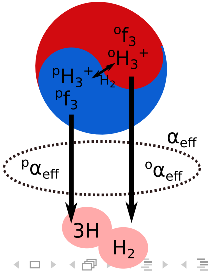
α_{bin}: binary recomb. rate co.

K_{He}: ternary (helium assisted) recombination rate coefficient

$\alpha_{eff} = \alpha_{bin} + K_{He}[He] + \ldots$

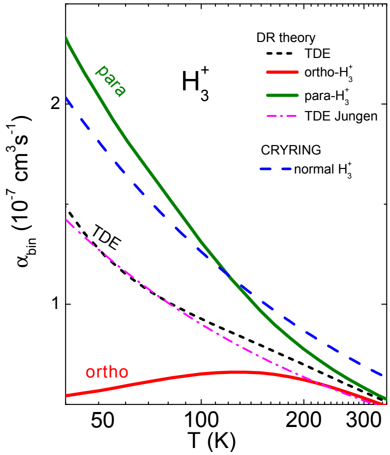
Recombination in a mixture of $^pH_3^+$ and $^oH_3^+$

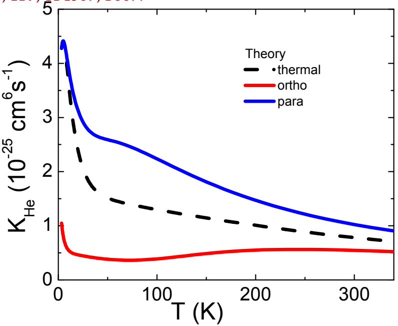
- $\alpha_{eff} = {}^p\alpha_{eff}{}^p f_3 + {}^o\alpha_{eff}{}^o f_3$
- NS conversion ${}^{p,o}H_3^+ + {}^{p,o}H_2$



Dependence of H_3^+-e recombination process on NSS

Jungen Ch., Pratt S. T., *Phys. Rev. Lett.*, **102**(2),023201,2009
Floresca dos Santos, S., V. Kokoouline & C. H. Greene. *J. Chem Phys.*, **127**, 124309, 2007.
Glosík J., Plašil R., Korolov I. et al., *Phys. Rev. A*, **79**(5),052707,2009
Petrignani A. et al, *Phys. Rev. A*,**83**, 032711,2011

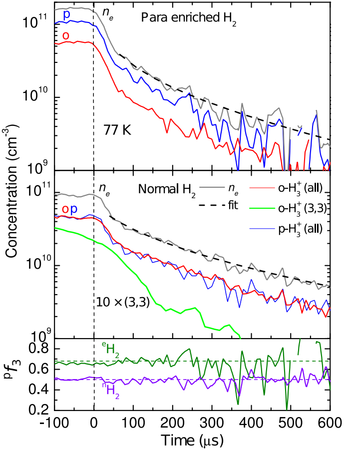




Theoretical predictions.
Measurements by storage rings – unspecified high rotational temperature.
Normal-H_3^+: ${}^{p}f_3$=0.5

Evaluation of recombination rate coefficients

We observe either $[H_3^+]$ or n_e in time



- We fit analytic solution of
  $$\frac{dn_e}{dt} = -\alpha_{eff} n_e^2 - \nu n_e$$
  to measured evolution of n_e or $[H_3^+]$
- Measurements with two different populations of para-H_3^+
  $$\begin{cases} \alpha_{eff}' = {}^pf_3' {}^p\alpha_{eff} + (1 - {}^pf_3') {}^o\alpha_{eff} \\ \alpha_{eff} = {}^pf_3 {}^p\alpha_{eff} + (1 - {}^pf_3) {}^o\alpha_{eff} \end{cases}$$
  2 equations with 2 variables ${}^p\alpha_{eff}$, ${}^o\alpha_{eff}$
- $\alpha_{bin} = \lim_{[He]\to 0} \alpha_{eff}$

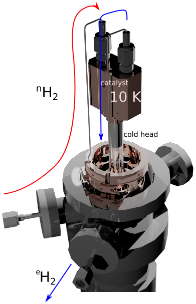
Varju J., Hejduk M., Dohnal P. et al., *Phys. Rev. Lett.*, **106**(20),203201,2011

Generation of H_3^+ ions in plasma

He, Ar, H_2 plasma

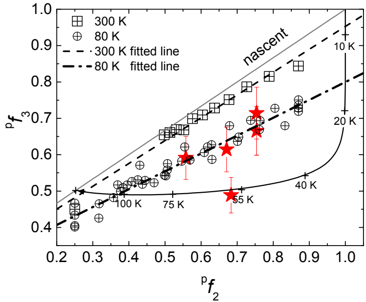
- $ArH^+ + {}^{p,o}H_2 \rightarrow {}^{p,o}H_3^+ + Ar$
- ${}^{p,o}H_2^+ + {}^{p,o}H_2 \rightarrow {}^{p,o}H_3^+ + H$ – Nascent distribution of NSS (selection rules)
- ${}^{p}f_3 = \frac{2}{3}\,{}^{p}f_2 + \frac{1}{3}$ We can change ${}^{p}f_3$ varying ${}^{p}f_2$.

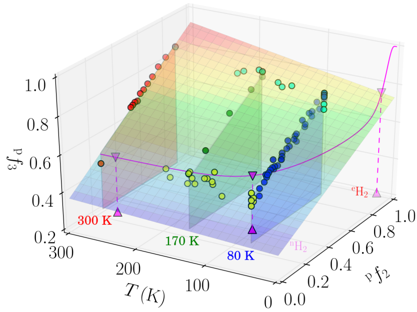
We use para-hydrogen generator to produce H_2 with abnormal fraction of para states (${}^{p}f_2 \geq 0.25$).



From nascent to final NSS distribution

$$^{p,o}H_3^+ + {}^{p,o}H_2 \longrightarrow {}^{o,p}H_3^+ + {}^{o,p}H_2$$



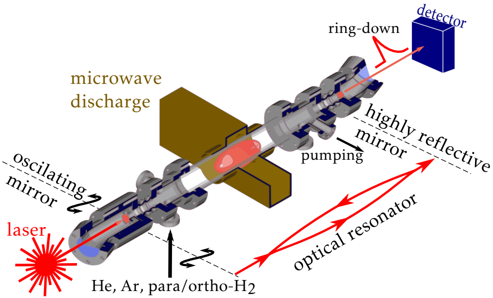


★: Astronomical observation, interstellar cloud in a direction of ζ Persei, X Persei etc.

Temperature dependence!

Crabtree, K. N. & McCall, B. J. Philosophical Trans. Royal Soc. A: Math., Phys. Eng. Sci. **370**, 5055–5065 (2012).
Grussie, F. et al. Astrophys. J. **759**, 21 (2012).

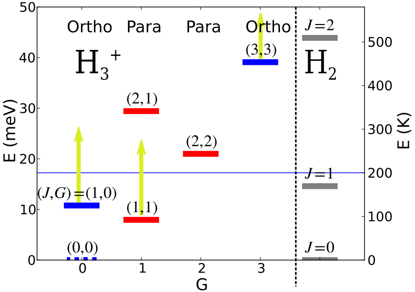
Apparatus – Stationary Afterglow in Cavity Ring-Down Spectroscopy apparatus (SA-CRDS)

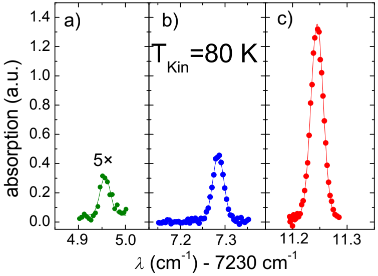


Stationary afterglow

- All reactants in discharge.
- Discharge tube cooled by LN_2 or its vapors to $77 < T < 200$ K.
- He/Ar/H_2 $10^{17}/10^{14}/10^{14}$ cm^{-3}

CRDS – monitored transitions





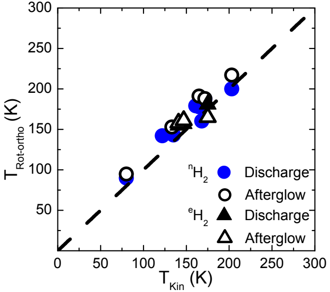
	transition	wave num. (cm^{-1})	NSS
a	$3\nu_2^1(4,3) \leftarrow 0\nu_2^0(3,3)$	7234.957	ortho
b	$3\nu_2^1(2,1) \leftarrow 0\nu_2^0(1,1)$	7237.285	para
c	$3\nu_2^1(2,0) \leftarrow 0\nu_2^0(1,0)$	7241.245	ortho

second overtone transitions

Hejduk M., Dohnal P., Varju J., *Plasma Sources Sci. Technol.*, **21**(2),024002,2012

CRDS – thermalization of rotational states within NS manifold

Populations of 2 rotational states of $^oH_3^+$ are monitored!

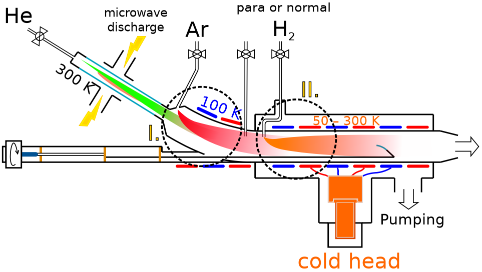


Already in the discharge!

Rotational temperature

- Experiment $\Rightarrow {}^{p}f_3(time) = const.$
- Each of para- and ortho-H_3^+ ensembles has own T_{Rot}.

Apparatus – Flowing Afterglow with Langmuir Probe (Cryo-FALP II)



Flowing afterglow – production of H_3^+-e^- plasma step by step

Regions

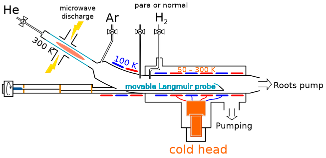
I. Ar^+ is dominant.

II. $ArH^+ + H_2 \rightarrow H_3^+ + Ar$

Experimental conditions

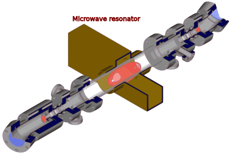
- $T = 50 - 300$ K.
- $[He] = 10^{17}\,cm^{-3}$, $[Ar] = 10^{14}\,cm^{-3}$ $[H_2] = 10^{12}\,cm^{-3}$.
- Langmuir probe diagnostics, electrons
- Gas velocity ≈ 10 m/s. space ↔ time.
- EEDF, electron temperature

Comparison of apparatuses



Cryo-FALP II

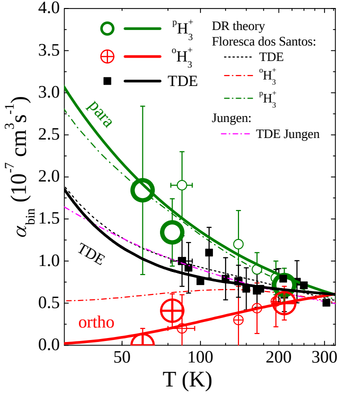
- $T = 50 - 300$ K
- Langmuir probe diagnostics: measurements of
  - n_e, i.e. concentration of all charged particles
  - EEDF

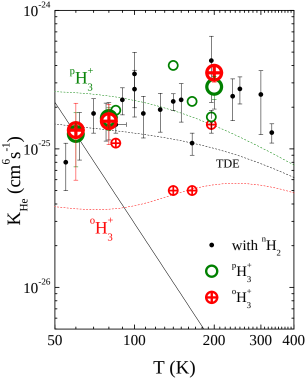


SA-CRDS

- $T = 77 - 300$ K
- absorption spectroscopy: measurements of
  - concentration of specific ions and neutrals
  - reaction kinetics of ions in specific states
  - internal temperatures of ions

Experimental results





Binary recomb. rate co.

agrees with the theory. A strong dependence on NSS.

Ternary recomb. rate co.

A strong dependence on NSS @ 150 K. Full black line: theory (D. R. Bates & S. P. Khare.*Proceedings of the Physical Society*, **85**, 231,1965).

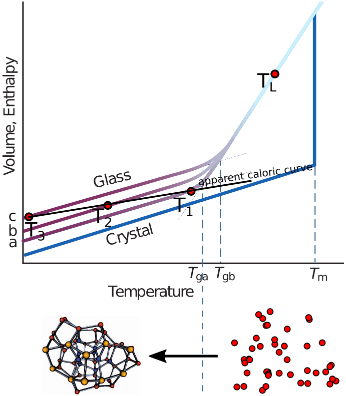
Rich world of reactions with water molecules

Studies of charged water clusters

- W. W. Duley, Molecular Clusters in Interstellar Clouds, The Astrophysical Journal, 471:L57–L60, 1996 – cited by only 3 articles
- Relatively simple to make:
  $$H_2O + \left\{ \begin{matrix} H_3^+ \\ H_2O^+ \end{matrix} \right\} \rightarrow H_3O^+ + \cdots$$
  $$H_3O^+ + H_2O\ (+\cdots) \rightarrow H^+(H_2O)_2\ (+\cdots)$$
- Rich chemistry:
  $$H^+(H_2O)_n + M \leftrightarrows MH^+(H_2O)_n^*$$
  formation of acids, various hydrocarbons, for example

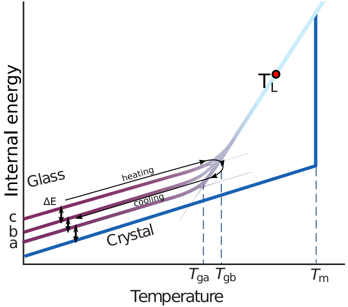
... AND THEY MAY RELEASE ENERGY IF HEATED AND COOLED

Nano-calorimetry



Nano-equivalent to amorphous ice

Glass phase of water clusters



$\Delta E \sim 1$ meV, explosive melting of comets

J. Matthew, W. Hosek et al., „Outburst dust production of comet 29p/Schwassmann-Wachmann 1“, The Astronomical Journal 145, 122 (2013)

Conclusion

We measured NSS-dependent rate coefficients of following reactions in last 3 years.

Para/ortho-$H_3^+ + e^-$

- $\rightarrow \begin{cases} H_2 + H \\ 3H \end{cases}$
- $+He \rightarrow \begin{cases} H_2 + H + He \\ 3H + He \end{cases}$

@ 60–300 K, 1st results with fully thermalised ensemble of H_3^+ ions.

$N^+(^3P_{j_a}) + \text{para/ortho-}H_2 \rightarrow NH^+ + H$

11–100 K, dependence on fine structure states.

$H^+ + \text{para/ortho-}H_2$

- $\rightarrow H_3^+ + h\nu$
- $+H_2 \rightarrow H_3^+ + H_2$

1st temperature dependence with regard to NSS.