Steady-state nuclear-spin chemistry in dark clouds

Pierre Hily-Blant
IPAG, Grenoble

A. Faure
C. Rist
G. Pineau des Forêts
D. R. Flower
M. C. Walmsley

Dedicated to
Malcolm C. Walmsley
Molecular clouds

Starless cores: a pivotal state

On the interstellar origin of nitrogen
From clouds to cores to planetary systems

- Physics of star and planet formation
- Chemical conditions in starless cores?
- Timescales of star formation?
Starless cores within molecular clouds
Physical conditions

- cold (10 K), dense \((n_H > 10^4 \text{ cm}^{-3})\)
- dark: \(A_V > 10\) mag (CR + UV from secondary photons)

Starless cores: chemical factories

PDR layer

Ice formation

CO freeze-out

Heavy freeze-out

Evaporation

C^+
CH
C_2H
OH^+
... HF

CO
NO
H_2O
OH
HCO^+
CS
N_2H^+, N_2D^+
CN
HCN
NH_3, NH_2D, ...
DCO^+

H_2D^+
D_2H^+
Completely depleted?

CO + highly volatiles

H_2O Organics

Visual extinction (mag)

Density of H (cm^{-3})

Gas kinetic temp. (K)

adapted from Bergin & Tafalla 2007
Molecular depletion

- Depletion affects most species
- Nitrogen bearing species (CN, NH$_3$, N$_2$H$^+$) less affected
  Hily-Blant et al. (2008)
- Complete depletion? Walmsley et al. (2004)
- Lightest species remain in the gas phase: H$_3^+$ and D-isotopologues
Tracing the inner parts

- Observations: usually one symmetry only: e.g. $\text{o-H}_2\text{D}^+$, $\text{p-D}_2\text{H}^+$, $\text{NH}_3$
- OPRs required to derive total column density

$o$-$\text{H}_2\text{D}^+$ at 372.4 GHz (Caselli et al. 2008), $\text{p-D}_2\text{H}^+$ at 692 GHz (Vastel et al. 2004)
Why OPRs are important?

- Derive total column densities
- Disentangle between formation pathways (Faure et al. 2013)
- Gas-phase vs surface chemistry
- Derive physical conditions and impact on thermodynamics

Can OPRs be used as astrochemical clocks?

- Updated network for the complete depletion scenario
- Time-dependent chemical calculations
- New network and preliminary results
OPR and deuteration

- Deuteration: $\text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2 + \Delta E$
- internal energy of o-$\text{H}_2$ promotes endoergic reactive collisions, mitigating deuterium fractionation
- Metals and electrons also decrease deuteration (destroy $\text{H}_2\text{D}^+$)
- Milestones: Dalgarno et al. (1973); Pagani et al. (1992); Gerlich et al. (2002); Walmsley et al. (2004)
- OPR of $\text{H}_2$ regulates deuteration, and OPR depends on timescale for NSC
- Idea: measure the deuteration to constrain the OPR of $\text{H}_2$
- Brünken et al. (2014): ortho and para $\text{H}_2\text{D}^+$ towards IRAS16293-2422; dense core chemical age $\sim 1$ Myr (Sipillä’s talk)
- Timescale for OPRs to reach steady-state: $\sim 1$ Myr (Flower et al. 2006; Kong et al. 2015; Furuya et al. 2015)
Timescale to reach steady-state

Initial conditions are lost after $\sim$ few $10^6$ yr
The OPR of $\text{H}_2$ in dense gas phase

- Competition between: formation on grain surfaces, spin conversion in the gas phase
- $\text{H}_2 + \text{XH}^+ \rightleftharpoons \text{H}_2 + \text{XH}^+$
- $\text{H}_3^+ + e^- \rightleftharpoons \text{H}_3^+ + e^-$
- $\text{H}_3^+ + \text{X} \rightleftharpoons \text{H}_2 + \text{XH}^+$

- Conversion in the gas phase: Hugo et al. (2009), state-to-state rates for $\text{H}_3^+ + \text{H}_2$ reactions
Thermalized OPR of $\text{H}_2$: $T_{\text{crit}}$

- Competition between formation on grains and gas-phase conversion
- Formation of $\text{o-} \text{H}_2$ from grains $\sim$ from $\text{p-} \text{H}_2$
- Thermalized ratios above $T_{\text{crit}} \approx 17$ K (Le Bourlot 1991; Flower et al. 2006)
New reaction rates

- Published rates: ground-state to species
- New rates *species-to-species*: averaging over Boltzman distribution of reactant populations

<table>
<thead>
<tr>
<th>Species A</th>
<th>Species B</th>
<th>Number of reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3^+$</td>
<td>HD $\text{H}_2$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{H}_2\text{D}^+$</td>
<td>HD $\text{H}_2$</td>
<td>61</td>
</tr>
<tr>
<td>$\text{D}_2\text{H}^+$</td>
<td>HD $\text{H}_2$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{D}_3^+$</td>
<td>HD $\text{H}_2$</td>
<td>67</td>
</tr>
</tbody>
</table>
- All OPRs thermalize above $T_{\text{crit}}$: leading role of $\text{H}_2$
- Discrepancy with previous rates larger for heavier species
- Reality: between the two extremes (ground-state and Boltzmann)
Thermalized OPRs

- Observed OPR of $\text{H}_2\text{D}^+$: $0.07 \pm 0.02$, 13–16 K, $t > 5(5)$ yr (Brünken et al. 2014)
- Fully compatible with steady-state predictions
• Depletion factor: $Z \times f$; density; initial conditions: atomic H
• Observations: strong depletion, $T = 12 − 16$ K, high densities
Steady-state OPRs in cores

- Initial conditions: $p$-$H_2$
- No constraint from $OPR(H_2D^+)$
• Timescales shorten with $n_H$
• Steady-state OPR decreases with $Z$
Steady-state OPRs

- Observed OPR of H$_2$D$^+$: reflects the age of H$_2$ since its (last ?) formation
- Minimum age of the embedding molecular cloud
- Bad news: does not tell the age of the core
- Good news: Results do not depend on the (unknown) initial conditions
The GRENOBLE network

- New network: hydrides of C, N, O, S; Deuterated N-hydrides
- Condensed network: 150 species, 1100 reactions
- Separated network: 205 species, 2900 reactions
- Separation program (spinstate.f90): automatic for exothermic; manual for thermoneutral and other specific reactions (e.g. $H_3^+ + e^-$)

The GRENOBLE model

- Chemical network (gas-phase, ads./des., surface chemistry)
- Self-consistently with Larson-Penston collapsing 1D, isothermal, core (plateau + $\rho \propto r^{-2}$ envelope)
- 1D-Radiative transfer
- Ray-tracing
Preliminary results: ammonia

H-MM1 NH₃(1,1)

Integrated intensity (K km/s)

Column density (cm⁻²)

N core

N env

N tot

N(NH3)env

N(NH3)core

N(NH3)tot

N_H2(core) (cm⁻³)

Obs. (Harju et al. 2016)
Preliminary results: ammonia

On the interstellar origin of nitrogen
Conclusions

• OPRs of $\text{H}_2$ and $\text{H}_3^+$ are in steady-state
• OPRs: measure the age of $\text{H}_2$

Perspectives

• Are all OPRs in steady-state?
• Modelling:
  • Self-consistent OPRs of C, N, O, and S hydrides
  • The D/H and OPR of water prior to protostar and disk formation
  • Tracers of the OPR of $\text{H}_2$
  • state-to-state chemistry
• Observations: ALMA
Physical Properties of Star Forming Regions

Malcolm Walmsley
Arcetri Observatory
Preliminary results

On the interstellar origin of nitrogen
References

Hugo, E., Asvany, O., & Schlemmer, S. 2009, JCP, 130, 164302