Theory of inelastic and reactive scattering

Gas phase quenching & reactivity
A decades-long venture of *IPAG* and several institutes in France and worldwide

**P. Valiron** L. WIESENFELD, A. FAURE, C. CECCARELLI, C. RIST

*V. Vuitton*

*N. TROSCOMPT, M. WERNLI, H MASSÓ F. DANIEL, E SAHNOUN*

Obs. Paris, Le Havre, Dijon, Lille,
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€ $ £ :
EU FP6 ‘Molecular Universe’, EU FP7,
Horizon 2020: COST ‘ The Chemical Cosmos’, *'Our Astrochemical History'*
CHESS KP Hershel Space Telescope  French Space agency (CNES),
ANR FORCOMS, **ANR HYDRIDES**, **CNRS (PCMI + others)**, LABEX OSUG@2020,
NWO (NL), JPL (NASA), MPE (GARCHING), **LABEX PALMS (Paris-Saclay)**
From observation to modelling

**On the sky**

- Line catalogs and characteristics

**Spectrum:** Line positions and shapes

- Photon emission, absorption, Receptor properties

**Abundances, speeds, Cartography**

**Image and/or interferogram reconstruction**

**Model:** chemistry, history

**Chemistry:** reactions thermodynamics and kinetics

*Interferogram: Beuther et al. (2007)*
A molecular physics perspective

Spectroscopic measures positions, intensities

Collisional properties computations/measures

Chemical species reactivity and kinetics

Spectral line position

Spectral line intensity

Chemical network

Parametric optimizations

Hydro or MHD codes

Observations in reactive gases, atmospheres, astrophysics gases

Non linear optics

Model for the object

Hamburg July 2017
A molecular physics perspective

Spectroscopic measures positions, intensities

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Parametric optimizations

Model for the object

Hydro or MHD codes
Thermodynamics vs kinetics (1)

- Why bothering?
  - For both internal degrees of freedom AND for abundances, most of the time, thermodynamics is not enough.
  - LTE: $T_{\text{internal}} = T_{\text{kinetic}}$
  - Critical density

- $n^*$ varies from $10^2$ to $10^{10}$ cm$^{-3}$ depending on frequency and internal motion

\[ n^* (\text{H}_2) = \frac{\sum A_{ij'}}{\sum k_{ij}} \quad (\text{cm}^{-3}) \]

Spontaneous emission (s$^{-1}$)

Collision rates (cm$^3$ s$^{-1}$)
Thermodynamics vs kinetics (2)

Why bothering?
Rates of reactions such that no thermodynamical equilibrium reached in general.

- \( k_{\text{Langevin}} \) : \( 10^{-7} \ldots 10^{-9} \text{ cm}^3/\text{sec} \) (ion-molecule)
- \( k_{\text{neutral}} \) : \( 10^{-10} \ldots 10^{-12} \text{ cm}^3/\text{sec} \) (radical-molecule)
- \( n(\text{H}_2) = 10^2 \ldots 10^6 \text{ cm}^{-3} \) Fractional abundance \( x < 10^{-5} \)
- Timescale > \( 10^8 \text{ sec} \) (\( \approx 10^2 \text{ years} \)) for fast ion-molecule (involving H) ... \( 10^{10} \text{ sec} \) for slower reactions

Compare with physical timescales for Star formation
\( 10^2 \text{ (shocks)} - 10^5 \ldots 10^7 \text{ years} \) : far to marginal for steady state / no thermodynamical equilibrium to be reached,
EXCEPT for dense disk forming regions + atmospheres.
Molecular Physics

SCATTERING

- Formalism well established, fairly well understood and tested
  - Very precise/quite versatile
- Bottlenecks
  - Quantum: number of coupled channels $|\alpha>$
  - Classical: ro-vibration quantization
- Limit:
  - Matrix size, limited by linear algebra LAPACK codes efficiency
  - State to state + higher temperatures
- Situation satisfactory for H/H2/e collisions, less so for heavy-heavy

REACTIONS

- Many formalisms no 'universal' code
- Classical codes useful for 'easy' cases, no state-to-state, ZPE not determinant
- Transition state theories very well developed, less so with tunneling
- Quantum codes VERY difficult, being it time independent or time dependent: channels, coordinates, energies
- Situation not satisfactory
Molecular inelastic collisions

HOW TO COMPUTE
Classical view, simple minded

Rotational quenching (& fine structure, hyperfine, ro-vibrational quenching) :
Transfer between projectile and target of kinetic energy /angular momentum (external and/or internal) + transient polarization

\[ J_1 \rightarrow J_2 \]

\[ l_{\text{orbital}} \]
Classical view, simple minded

• $l_{\text{orbital}} = p \ b = m \ \nu \ b$

(m reduced mass; b impact parameter; $\nu$ relative velocity)

Exchange $l \leftrightarrow J$ makes LTE
How to compute collisional rate of transfer?

Definition of the problem
- Which molecule, at what energy/temperature, which motion (rotation/torsion/vibration)?

Potential energy surface
- Ab initio method, precision, long and short distance
- Fit

Dynamics
- Classical (canonical, T defined): Quantum (micro-canonical, E defined)

S matrices / trajectories
- Sums & average to get sections, rates, DCS, Pressure broadening/shift
Tackling with collisional problem in three stages:

1. Computing interaction of molecule and H$_2$/He: ab initio quantum chemistry.
   → Potential at N points

2. Fitting N points onto one functional $F(R, \text{angles})$

3. Performing quantum or classical scattering

Potential energy surface (Force field, classically thinking)

Dynamical calculation
HNCO:
A recent example

**HNCO in the Galactic Centre**

The $1_01-0_00$ transition of the HNCO molecule at 21.9817 GHz has been detected using a 1.4 cm parametric amplifier at the 36 foot telescope of the US National Radio Astronomy Observatory. The present observations were made with the

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**David Buhl**  
National Radio Astronomy Observatory,  
Green Bank, West Virginia  

**Lewis E. Snyder**  
University of Virginia,  
Charlottesville, Virginia  

**Philip R. Schwartz**  
E. O. Hulbert Center for Space Research,  
Naval Research Laboratory,  
Washington, DC  

**Jochen Edrich**  
University of Denver,  
Denver, Colorado  

Received May 21, 1973.

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**NATURE VOL. 243 JUNE 29 1973**
The Harmonic Force Field and $r_z$ Structure of HNCO

Luciano Fusina and Ian M. Mills

Fig. 1. Structural parameters and vibrational symmetry coordinates for the harmonic force field of HNCO. The structure used in the force field calculation was: $r$(NH) = 0.986 Å, $\Theta$(HNC) = 128.0°, $r$(CN) = 1.209 Å, $\Theta$(NCO) = 170.0°, $r$(CO) = 1.116 Å. The symmetry coordinates are all defined as

Experimental geometry: planar.

Vibrational frequencies

$\nu_5 = 577.5$ cm$^{-1}$ (HNC bend)
$\nu_6 = 659.8$ cm$^{-1}$ (torsional)

Rigid approximation valid at moderate temperatures ($T \lesssim 200$K)
Spectroscopy

Energy (cm$^{-1}$) vs. $K_C$

HNCO levels, $J_{KaKc}$

Transition $\leq$ 300GHz

Transition $>$ 300GHz
HNCO in a protostar, IRAS16293

Caux et al., unpublished results 2016
PES HNCO – H₂

\[\text{HNCO} - \text{H}_2\]
De-excitation cross sections

HNCO – para H2 CC and CS scattering. E. Sahnoun, LW et al.;, unpub. results

Dipolar transitions

Transitions to ground state

1 -> 0
2 -> 0
3 -> 0
4 -> 0
De-excitation rates

HNCO – para H2 CC and CS scattering
Figure 2. Rate coefficients for the quenching of CO($J_2 = 5$) by collisions with para-$H_2$ as functions of temperature. Lines indicate present calculations on potential $V_{04}$, symbols denote the results of Flower (2001) on potential $V_{03}$. Solid line and solid circles: $J_2 = 5 \rightarrow J_2' = 0$, dotted line and open circles: $J_2 = 5 \rightarrow J_2' = 1$, dashed line and solid squares: $J_2 = 5 \rightarrow J_2' = 2$, dot-dashed line and open squares: $J_2 = 5 \rightarrow J_2' = 3$, long-dashed line and solid triangles: $J_2 = 5 \rightarrow J_2' = 4$. 
EXCITATION OF INTERSTELLAR HYDROGEN CHLORIDE

DAVID A. NEUFELD
Johns Hopkins University, Department of Physics and Astronomy, 3400 North Charles Street, Baltimore, MD 21218

AND

SHELDON GREEN
NASA/Goddard Space Flight Center, Institute for Space Studies, 2880 Broadway, New York, NY 10025

Received 1993 October 25; accepted 1994 February 25

EXCITATION OF HCl

TABLE 1

RATE COEFFICIENTS FOR COLLISIONAL EXCITATION OF HCl BY He (cm$^3$ s$^{-1}$)

<table>
<thead>
<tr>
<th>$J_f$-$J_i$</th>
<th>10 K</th>
<th>20 K</th>
<th>30 K</th>
<th>50 K</th>
<th>80 K</th>
<th>100 K</th>
<th>200 K</th>
<th>300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0 .......</td>
<td>3.35 $(-12)^a$</td>
<td>4.20 $(-12)$</td>
<td>5.09 $(-12)$</td>
<td>6.88 $(-12)$</td>
<td>9.29 $(-12)$</td>
<td>1.07 $(-11)$</td>
<td>1.54 $(-11)$</td>
<td>1.80 $(-11)$</td>
</tr>
<tr>
<td>0-0 .......</td>
<td>7.18 $(-12)$</td>
<td>8.80 $(-12)$</td>
<td>1.09 $(-12)$</td>
<td>1.60 $(-12)$</td>
<td>2.07 $(-12)$</td>
<td>2.71 $(-13)$</td>
<td>3.56 $(-13)$</td>
<td>4.58 $(-13)$</td>
</tr>
</tbody>
</table>

*Estimated accuracy: 10%
Simpler computations

HCl

Lanza, Lique, LW et al 2014

064316-9 Lanza et al.

FIG. 11. Cross sections for selected transitions out of $\text{HCl}(j_1 = 7)$. 

FIG. 1. The body-fixed $J$
Three cases:

- **H2O** ↔ Great importance chemically + observations be Herschel + isotopologues

- **HCO+/DCO+**  Main molecular ion; very deep and long-range potential,

- **NH3** Thermometer + isotopologues
Cross sections, HDO-H$_2$

$\sigma (E_{\text{collision}})$

More complicated rotational structure H$_2$O

HDO – H$_2$: Example of rates

Collisional excitation of doubly and triply deuterated ammonia ND$_2$H and ND$_3$ by H$_2$.

F. Daniel$^{1*}$, C. Rist,$^1$ A. Faure,$^1$ E. Roueff,$^2$ M. Gérin,$^3$ D.C. Lis,$^{4,5}$ P. Hily–Blant,$^1$ A. Bacmann$^1$ and L. Wiesenfeld$^1$

Figure 3. Cross sections for $\alpha$-ND$_3$ that originate from the $1_1^-$ level. This figure can directly be compared to Fig. 13 of Ma et al. (2015) and the cross sections obtained in the latter study are reported as dotted lines.
More complicated energetic structure

HCO+

Min V = -1487.5 cm⁻¹

Elastic and inelastic ($\Delta J < 0$) sections

Helium: comparison with Buffa et al., 2009
Vibrational excitation:
CO, CH3OH, H2O

LW, J Hutson, M. Gonzalez, WF Thi CC, unpublished results

Ro-vibrational deexcitation of H2O
V_b=1 → V_b=0
3 PES
J(H2)=1,3,5; J(H2O)≤ 16; J total J = 20 (One partial wave)

==================================
m_H2O+H2_asrot ORTHO-H2O-ortho-H2 |
Valiron 6d PES
==================================

TOTAL ANGULAR MOMENTUM, JTOT = 20
SYMMETRY BLOCK = 1
N = 7964

COUPLED CHANNEL MOLECULAR SCATTERING PROGRAM OF J. M. HUTSON AND S. GREEN, VERSION 14 (MAR 95)  |
|  |
|  |
|  THIS RUN USED 315817.91 CPU SECS AND********** OF THE |
|  ALLOCATED********** WORDS OF STORAGE |
|  ELAPSED TIME 62973.97 CLK SECS |
|  |
|  DONE ON 24/02/2016 AT 10:51:15 FROM HOST ccas30 |
Other properties

- Pressure broadening $\rightarrow$ H2O
- Collision induced absorption $\rightarrow$ N2-N2
Pressure broadening

Baranger, 1958:

Therefore, the width becomes

\[
\omega = \left\{ \frac{1}{2} n v \left[ \sigma_{i\text{ in}} + \sigma_{f\text{ in}} + \int d\Omega \left| f_i(\Omega) - f_f(\Omega) \right|^2 \right] \right\}_{\text{Av}},
\]

Sums of inelastic cross-sections

Interference between elastic amplitudes

The interference term way more difficult: elastic amplitudes. Neglect at ‘high’ temperatures.
No free parameter: comparison of absolute scales
Pressure-Broadening and line shift theory vs experiments
A short bibliographic subjective view

REACTIVITY
Why so much more difficult

**PES**
- Geometry:
  - multidimensional: $\text{dim} = 3N-6$
  - Many reactive channels
  - More 'hilly': many TS, metable intermediates
- If open-shell:
  - multi-configurational, much more difficult on the ab initio point of view
  - Co-existence of several symmetries, spin states
  - Importance of magnetic (spin-orbit) transitions

**Dynamics**
- Classical dynamics:
  - Often precise and reliable on ONE surface, for overall rates/branching ratios
  - Difficult treatment of ZPE/symmetries
  - Treatment of multiple surface (surface hopping) ad hoc at best.
- Quantum dynamics
  - Time independent: Very tough, but doable for 3 atoms. very precise, includes all effects.
  - Ti
PES for reactivity

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_A nine-dimensional ab initio global potential energy surface for the \( \text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H} \) reaction_

Ayang Li and Hua Guo
A nine-dimensional ab initio global potential energy surface for the H2O+ + H2 → H3O+ + H reaction

Anyang Li and Hua Guo
PES for reactivity

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\[ \text{H da Silva, thesis, 2017, U Paris-Saclay.} \]
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  • Often precise and reliable on ONE surface, for overall rates/branching ratios
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• TST very powerful
• Quantum dynamics
  • Time independent: Very tough, but doable for 3 atoms. Very precise, includes all effects.
  • Time dependant could be a path towards results.

Figure 1. The rate constant of the reaction CN + NH$_3$ as a function of temperature. The capture prediction, eq 1, is given by the dashed line and stars denote values at 10 and 30 K. The data from the CRESU experiment is represented by the filled circles. The present model is denoted by the solid line.
Dynamics

- Classical dynamics:
  - Precise and reliable on one surface, for overall rates/branching.
  - Difficult treatment of ZPE/symmetries.
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- TST very powerful.

Quantum dynamics:
- Time independent: Very tough, but doable for 3 atoms. Very precise, includes all effects.
- Time dependent could be a path towards results.

Figure 3. The initial state ($v_i = 0, j_i = 1$)-specified ICSs (upper panel) and rate constants (lower panel) obtained by exact partial wave summation and an interpolation method (see text for detail). The rate constant obtained from the J-shifting model is also included in the lower panel.
FIG. 2. Total reaction probability, as a function of collision energy, for the O(1D) + H–CH3(v = 0, j = 0) → CH3 + OH reaction at J = 0.

Published in: R. Ben Bouchrit; M. Jorfi; D. Ben Abdallah; N. Jaidane; M. González; B. Bussery-Honvault; P. Honvault; *The Journal of Chemical Physics* 2014, 140, DOI: 10.1063/1.4885276
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FIG. 3. TIQM vibrationally state-resolved reaction probabilities, as a function of collision energy, for the O(1D) + H–CH3(v = 0, j = 0) → CH3 + OH(v′) reaction at J = 0.
FIG. 8. Rate coefficient, in cm$^3$ molecule$^{-1}$ s$^{-1}$, as a function of the temperature. Solid line, TIQM (this work), dashed line and square symbols, QCT;36 circle symbols, experimental results 26–29
Conclusion
Back to experiments, computing and modelling....