Cold Molecules: Why? How? And Next?
Modeling routes for their formation
Olivier Dulieu

Laboratoire Aimé Cotton, CNRS/Université Paris-Sud/ ENS Cachan Orsay, France
Laboratoire Aimé Cotton in Orsay
Staff:
Nadia Bouloufa, Olivier Dulieu, Maxence Lepers, Goulven Quéméner, Maurice Raoult, Jacques Robert

PhD:
Dimitri Borsalino, Humberto da Silva Jr

Postdocs:
Maykel Gonzalez-Martinez, Andrea Orban, Romain Vexiau

Emeritus:
Anne Crubellier, Eliane Luc, Jean-François Wyart

*They left the group in 2013-2014:*
Mireille Aymar, Jesus Perez-Rios, Gaoren Wang
ONGOING PROJECTS @ LAC.THEOMOL

Structure of lanthanides (Er, Dy,...) and of small molecules (A-Sr), (A-Sr)⁺, Rb-(Ca⁺, Ba⁺, Yb⁺)... 

Long-range interactions between atoms and molecules

Formation/production of cold molecules

Structure and dynamics of cold atoms and molecules

Collisional processes in the interstellar medium

Dynamics of ultracold gases in external fields

Dynamics of cold molecular ions

Formation/production of cold molecules
WHY?
How cold ...?

Looking at collision processes over 10 orders of magnitude of kinetic energy/temperature.

Translational kinetic energy:
- 6000 K (vibration)
- 100 K (rotation)
- 0.1 K (hyperfine)
- 38 µK (translation)
- 200 nK

How cold ...

Cold molecules

Ultracold molecules
BUT with high internal energy

Adapted from Ye's group; http://jila.colorado.edu/yelabs/research/ultracold-molecules
Cold Matter: Atoms, Ions, Molecules, Plasmas…
almost $0 < T < 1K$

- One of the main research topic in AMO physics for many years: full control of a quantum system at the single quantum level
- Connected to many areas: statistical physics, condensed matter, optics, metrology,…
- Boosted by the amazing success of laser cooling and evaporative cooling

Nowadays applied to many atomic species: Alkalis, alkaline-earth, rare gas, lanthanides,…

**Molecules** are attractive for cold matter:
- Additional degrees of freedom, offering new opportunities for manipulation and control
- Pair of weakly interacting atoms for unprecedented precision measurements
- Reactivity and chemical reactions dominated by quantum effects (resonances, tunneling,…)
- Ongoing efforts to create dense ensembles of cold molecules
- Strong interplay between experiment and theory

- But direct laser cooling almost impossible!
A brief guide to cold molecule formation methods...

- **Assemble ultracold atoms:**
  - Photoassociation
  - Magnetoassociation

**T << 1 mK**
- Create stable molecules in (a single) excited level
- Transfer to the absolute ground state: adiabatic transfer (STIRAP), shaped laser pulses,...

**OR**

- **Slow down preformed molecules** with external time varying electric or magnetic fields through their intrinsic dipole moments, or via collisions with a buffer gas

**T > 1 mK**
- Let atoms stick together on/in helium nanodroplets

**T ~ 1 K**
- **Laser-cool** species with suitable properties (SrF, Yo,...) >CaH⁺...

**OR**

**T ~ 1 mK**
- ...

(mostly diatomics...)

---

Thé OMOI

LAbORATOIRE Aimé Cotton

CNRS SUD

UNIVERSITÉ PARIS SUD

ENS CACHAN
Cold Molecules: a hot topic indeed!
...
Outline

• (brief) Overview of methods and tools to describe an ultracold molecule

• Formation of ultracold ground state molecules via STIRAP

• Formation of ultracold molecular ions in merged atom/ion traps
HOW...

to describe a molecule?
A diatomic molecule is...

\[ \propto \frac{C_6}{R^6} \]

\[ D_{ge}(R) \]

\[ \propto \frac{C_3}{R^3} \]

or

\[ \propto \frac{C_6}{R^6} \]

Ground state

Excited state

Chemical bond

\[ \frac{\vec{E}}{\vec{D}(R)} \]
The Born-Oppenheimer approximation

\[ H = -\frac{\hbar^2}{2\mu} \nabla^2_R - \frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V \]

Electronic Hamiltonian

- \frac{\hbar^2}{2\mu} \nabla^2_R = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{O^2}{2\mu R^2}

Relative motion of the nuclei

Adiabatic Potential Energy Curves:
\[ R \rightarrow \infty: \text{Separated atoms} \]

Total wave function
\[ \Psi_{BO}^{(\alpha)} = \psi^{(\alpha)}(\vec{R}) \phi_{\alpha}(R; \vec{r}_i) \]

Molecular symmetries

Hund's cases

\[ \frac{J^2}{2\mu R^2} + \frac{L^2 - 2\vec{L} \cdot \vec{J}}{2\mu R^2} \]

Rotation Coriolis

\[ \left[ \begin{array}{c} 2S + 1 \Lambda \sigma_p \end{array} \right]_\Omega : |\alpha, \Omega \rangle \equiv |\alpha, \Lambda, S, \Sigma \rangle, \Omega = |\Lambda + \Sigma \rangle \]

\[ \Omega \sigma_p : |\alpha, \Omega \rangle \equiv \{ 0^+_g, 0^-_g, 0^+_u, 0^-_u, 1^-_g, 1^-_u, \ldots \} \]
Calculation of potential energy curves in the « chemical range »
A tough many-body problem! A scientific area in itself: Quantum Chemistry

- Ex: Cs$_2$: 2 nuclei and 110 electrons!

- In the case of alkali atoms and alkaline-earth atomic ions, a great simplification can be made: Atom/Ion treated as an effective one-electron system: Use of ECP's (Effective core potentials or pseudopotentials) with $\ell$–dependent CPP’s (core-polarization potentials) fitted on atomic energy spectra of the one-electron system

- [ECP+CPP+1e$^-$]+[ECP'+CPP'+1e$^-$]: exact energy at $R=\infty$

Typical steps are (in an oversimplified way):

- Choose a set of basis functions appropriate for numerical calculations: Gaussian orbitals
- Determine one-electron molecular orbitals through a self-consistent field approach (Hartree-Fock): describes the motion of one electron in the field of the cores and of the other electrons
- Set up a configuration space with antisymmetrized spin-orbital wave functions built on the HF orbitals
- Diagonalize the Hamiltonian (Full Configuration Interaction (FCI)) to determine the structure of the dimer, considered as an effective two/three-electron polarizable system
- Convergence and accuracy checked against size of basis sets, and through detailed comparison with other methods
- Potential energy curves, permanent and transition dipole moments, static and dynamic dipole polarizabilities,...
Calculation of potential energy curves in the asymptotic range

A well-known “electrostatic” problem!

- In a cold atom gas, the kinetic energy of the atoms is much smaller than any other characteristic energy (electronic, vibrational, rotational...), thus they feel each other at very large distances, well beyond the range of chemical interaction (exchange forces).
- $V_0$ overlap between the electronic wave functions of each atom.
- Potential energy determined by atomic properties.

Multipolar expansion of the electrostatic interaction:

Interaction of two charge distributions at large distances

$$V_{el} = \frac{1}{4\pi\varepsilon_0} \sum_{L_A, L_B = 0}^{+\infty} \frac{V_{L_AL_B}}{R^{1+L_A+L_B}}$$
1. Electrostatic potential generated by A in a remote point O'
2. Potential energy felt by B due to the slowly-varying field created by A
3. Potential energy between A and B

\[
V_{el} = \frac{1}{4\pi\varepsilon_0} \sum_{L_A, L_B = 0}^{+\infty} \sum_{M = -L_\leq}^{+L_\leq} \frac{f_{L_A L_B M}}{R^{1+L_A+L_B}} Q_L^A Q_{-L}^B \quad \text{with} \quad L_\leq = \min(L_A; L_B)
\]

\((L_A, L_B)\) : rank of multipolar moments of A et B
- \((0,0)\) : charge-charge interaction \(\alpha \ 1/R\)
- \((1,0)\) : dipole-charge interaction \(\alpha \ 1/R^2\)
- \((1,1)\) : dipole-dipole interaction \(\alpha \ 1/R^3\)
- \((0,2)\) : charge-quadrupole interaction \(\alpha \ 1/R^3\) ...
\[ \hat{V}_{el} = \frac{1}{4\pi\varepsilon_0} \sum_{L_A, L_B=0}^{+\infty} \sum_{M=-L}^{+L} \frac{f_{L_AL_B^M}}{R^{1+L_A+L_B}} \hat{Q}_L^M \hat{Q}_{L_B}^{-M} \]

- **1st order**: permanent multipoles

\[ \varepsilon^1_p = \langle \varphi^0_p | \hat{V}_{el} | \varphi^0_p \rangle = \frac{1}{4\pi\varepsilon_0} \sum_{L_A, L_B=0}^{+\infty} \sum_{M=-L}^{+L} \frac{f_{L_AL_B^M}}{R^{1+L_A+L_B}} \langle \Phi_A | \hat{Q}_L^M | \Phi_A \rangle \langle \Phi_B | \hat{Q}_{L_B}^{-M} | \Phi_B \rangle \]

- Ex: 2 neutral non-S atoms => dominant term = \( V_{qq} \sim 1/R^5 \)
- Ex: 2 neutral S atoms => \( \varepsilon^1_p = 0 \)

- **2nd order**: induced multipoles

\[ \varepsilon^2_p = - \sum_{(a,b) \neq (A,B)} \left[ \frac{\langle \Phi_A | \langle \Phi_B | \hat{V}_{el} | \Phi_a \rangle | \Phi_b \rangle \rangle^2}{(E_a - E_A) + (E_b - E_B)} \right] \]

- Ex: dipolar interaction = \( V_{dd}^{(2)} \sim 1/R^6 \) (van der Waals)
Example: structure of alkali dimers

Adapted from Jones et al, RMP 2006, Weiner et al, RMP 1999

Observation of Pure Long-Range Molecules
Predicted by Uang et al, PRL 1978

Hyperfine structure

Aldeguende et al PRA 79, 013401 (2009)
Features of the radial motion


\[
\begin{align*}
\alpha_L(k) &= \frac{-\tan \delta_L}{\frac{\lambda}{4\pi a^2}} \\
\sigma(k) &= \frac{4\pi a^2}{1 + a^2 k^2}
\end{align*}
\]
HOW... to create a cold molecule?
Laser Cooling of Molecules...not so cool!

Laser cooling of molecules: A sequential scheme for rotation, translation, and vibration

J. T. Bahns, W. C. Stwalley, and P. L. Gould
Department of Physics, University of Connecticut, Storrs, Connecticut 06269-3046

A novel scheme is proposed for sequential cooling of rotation, translation, and vibration of molecules. More generally, this scheme manipulates and controls the states and energies of molecules. The scheme, while somewhat complex, is simpler and more feasible than simply providing a large number of synchronously but independently tunable lasers. The key component is a multiple single frequency laser in which a single narrow band pump laser generates an ensemble of resonant “stimulated Raman” sidebands subsequently amplified and selected in a sample of the molecules to be cooled….Only this specific order of rotation–translation–vibration appears feasible (using molecules produced by photoassociation of ultracold atoms avoids the requirement for translational cooling). Each step employs true dissipative cooling ... by spontaneous emission and should yield a large translationally cold sample of molecules in the lowest \( v=0, J=0 \) level of the ground electronic state…

« ground-breaking » idea: photoassociation of cold atoms...
Photoassociation of cold atoms + radiative stabilization

Seminal papers on cold atom PA:

First observations of ultracold molecules
Cs\(_2\): Orsay, PRL, 80, 4402 (1998);
Rb\(_2\): Pisa, PRL, 84, 2814 (2000)

... But not selective in the final states...

Transfer density of probability inwards to produce (deeply-bound) ultracold molecules...
Cold molecule formation: Feshbach resonances, Magnetoassociation

- Atoms with electronic AND nuclear magnetic moments (alkalis, lanthanides, ...)
- First pointed out by Stwalley (PRL 37, 1628, 1976) and Tiesinga et al (PRA 47, 4147, 1993)
- The magnetic moment of a molecular complex and of an atom pair are different, so that their energy vary differently with magnetic field
- Change of the dissociation energy of a high-lying molecular bound state
- Very powerful method for creating (weakly-bound) ultracold molecules!

From www.uibk.ac.at

Chin et al, RMP 2012
Cold molecule formation: energy relaxation toward the absolute ground level

STIRAP: STImulated Raman Adiabatic Passage (Bergman 1990)

Determine **the most efficient STIRAP scheme** in order to create ultracold molecules in their absolute ground state.

Efficiency: strongly depends on the detailed characteristics of the system AND of the lasers available in the lab.

Achieved in an optical lattice to avoid atomic and molecular collisions.
Full modeling of STIRAP in KRb

See experiments by J. Ye and D. Jin at JILA

PRA 90, 033413 (2014)
Full modeling of STIRAP in KRb

Assuming
\[ \Omega_{\text{pump}} = \Omega_{\text{dump}} \]
\[ I_{\text{pump}} = I_{\text{dump}} \]

Dump transition energy to \( v=0 \) (cm\(^{-1}\))

Pump transition energy from \( v_a \) (cm\(^{-1}\))

PRA 90, 033413 (2014)
Full modeling of STIRAP in KRb

Assuming

\[ \Omega_{\text{pump}} = \Omega_{\text{dump}} \]

\[ I_{\text{pump}} = I_{\text{dump}} \]
Full modeling of STIRAP in KCs

Assuming
\[ \Omega_{\text{pump}} = \Omega_{\text{dump}} \]
\[ I_{\text{pump}} = I_{\text{dump}} \]

Full modeling of STIRAP in KCs

Optical trapping of ultracold molecules

Knowledge of molecular data: \( \text{Cs}_2 \) \( v=0 \) of the ground state

\[
U_{\text{dip}} = -\frac{1}{2\varepsilon_0 c} \text{Re}(\alpha) I, \quad \Gamma = \frac{1}{\hbar\varepsilon_0 c} \text{Im}(\alpha) I
\]

\[
\alpha_i(\omega) = 2 \sum_f \frac{\omega_{if} - i\gamma_f/2}{(\omega_{if} - i\gamma_f/2)^2 - \omega^2} \left| \langle f | d(R)\hat{R}.\hat{e} | i \rangle \right|^2.
\]

Strongly resonant patterns:
- Suppression of resonant regime due to unfavorable FC
- Resonant regime
- Off-resonant regime: smooth variation

Magic wavelengths for atom and molecule trapping

Identical trapping conditions (same polarizability) for initial and final states

Good matching of the motional states in the lattice

Cs$_2$ v=0 of the ground state

Rb$_2$ v=0 of the lowest triplet state
And NEXT...?
Merging laser-cooled atoms and ions: hybrid traps

The hybrid trap at University of Basel (Willitsch’ group)

Resonant-excitation mass spectrometry
Drewsen et al PRL 93, 240201 (2014)
Cold molecular ion formation by radiative association

\[
\sigma^{\text{RCT}}(e_i) = \frac{8\pi^2}{3c^3} \frac{1}{k_i^2} \sum_{J=0}^{\infty} \int \left[ \omega_{i_f}^3 J \langle J - 1, e_f | D(R) | e_i, J \rangle^2 \right] \] \[+ \left( \omega_{i_f}^3 (J + 1) | \langle J + 1, e_f | D(R) | e_i, J \rangle |^2 \right] \] \] \[d e_f,
\]

\[
\sigma^{\text{RA}}(e_i) = \frac{8\pi^2}{3c^3} \frac{1}{k_i^2} \sum_{J=0}^{\infty} \sum_{\nu=0}^{\nu_{\text{max}}} \left[ \omega_{i_f, \nu}^3 (J - 1) \langle J - 1, \nu | D(R) | e_i, J \rangle^2 \right] \] \[+ \left( \omega_{i_f, \nu}^3 (J + 1) | \langle J + 1, \nu | D(R) | e_i, J \rangle |^2 \right] \] \]

Cold molecular ion formation by radiative association

Cold molecular ion formation by radiative association

Strongly (polar) magnetic molecules made of Erbium

arXiv:1504.04578

Ultracold polar molecules composed of strongly magnetic atoms

A. Frisch,1, 2 M. Mark,1 K. Aikawa,1,* S. Baier,1 R. Grimm,1, 2 A. Petrov,3, †
S. Kotochigova,3 G. Quéméner,4 M. Lepers,4 O. Dulieu,4 and F. Ferlaino1, 2

1Institut für Experimentalphysik und Zentrum für Quantenphysik,
Universität Innsbruck, Technikerstrasse 25, 6020 Innsbruck, Austria
2Institut für Quantenoptik und Quanteninformation,
Österreichische Akademie der Wissenschaften, 6020 Innsbruck, Austria
3Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA
4Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, ENS Cachan, 91405 Orsay, France
Merci, Thank you
Anisotropic effect in collisions of ultracold polar molecules

Figure 74. Quantized stereodynamics of ultracold chemical reactions in quasi-two dimensions. (a) A quasi-2D geometry for collisions is realized for polar molecules confined in a 1D optical lattice. An external electric field is applied along the tight confinement axis. (b) Schematic showing the three lowest adiabatic potentials for collisions as a function of the intermolecular separation, \( R \). (c) Schematic showing each individual case for the three lowest collision channels. Reprinted with permission from ref 155. Copyright 2011 Nature Publishing Group.

Figure 76. Measurements of 2D loss rates and comparison with theory. (a) A fit (solid lines) to the measured loss curves, with (red circles) and without (black squares) 0.3 ms of parametric heating in \( \hat{z} \), is used to extract the loss-rate constants \( \beta_{(3)} \) and \( \beta_{(2)} \). (b) The extracted loss-rate constants for collisions of molecules in the same lattice vibrational level (black squares) and from different lattice vibrational levels (red circles) plotted for several dipole moments. Measured loss-rate constants for molecules prepared in different internal states are shown as green triangles. The solid lines represent the results of a quantum scattering calculation. (See Figure 74b and 74c.) Reprinted with permission from ref 155. Copyright 2011 Nature Publishing Group.
Full quantum treatment of atom-molecule collisions...

Figure 40. Adiabatic energies as a function of the hyperspherical radius $\rho$ for the lowest quartet state of the $^7$Li$_3$ potential energy surface.
Laser-cooling of molecules...finally!

2D Magneto-Optical Trapping of Diatomic Molecules

Matthew T. Hummon, Mark Yeo, Benjamin K. Stuhl, Alejandra L. Collopy, Yong Xia, and Jun Ye

YO molecule

SrF molecule
Molecules and ultracold matter

« The field of cold and ultracold molecules has recently witnessed a number of spectacular advances reliant upon the high quality of our knowledge of molecular structure at a very fundamental level. This lecture will illustrate this premise, highlighting the characteristics of molecules that we all care about. »
Scattering length:
a crucial parameter for cold collisions

Asymptotic wave function:
\[ \psi_L(r) \sim r \to \infty \sin(kr - L\pi/2 + \delta_L) \]

Scattering amplitude in elastic collisions
\[ f(\Theta) = \frac{1}{2ik} \sum_{L=0}^{\infty} (2L + 1)(e^{2i\delta_L} - 1)P_L(\cos \Theta) \]

Elastic cross section
\[ \sigma = \frac{4\pi}{k^2} \sum_{L=0}^{\infty} (2L + 1) \sin^2 \delta_L \]

Scattering length: \[ a_L(k) = -\tan \delta_L \]
Cold collisions: \[ \sigma(k) = \frac{4\pi a^2}{1 + a^2 k^2} \]

The dynamics is fully determined by a global parameter for the interaction: \( a \)

This has important consequences for achievement of quantum degeneracy of ultracold gases