COLD MOLECULE AND PHOTOASSOCIATION

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WHAT IS COLD MOLECULE?

- A neutral bound system with more than one atom has a very low kinetic energy (translational, vibrational, rotational)

- \( \text{K}_2, \text{KRb}, \text{Rb}_2, \text{Cs}_2 \ldots \)

New problems in molecular system
WHY COLD MOLECULE?

- **Fundamental research**: fundamental constant, EDM, PNC
- **New era of chemistry**: superchemistry
- **Quantum simulator** for solid state physics
- **Quantum Computer**
TEMPERATURE, DENSITY AND COOLING

Table 1. Orders of magnitude estimate of the phase space density and temperature of molecular ensembles required to achieve the main scientific goals that stimulate the development of ultracold molecule research. For dipolar physics, we assume a permanent dipole moment of $x \text{ Debye}$. The molecular mass is assumed to be $x \text{amu}$. The following table provides estimates for different scientific goals:

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<tr>
<th>Phase Space Number</th>
<th>Scientific Goal</th>
<th>Temperature Goal</th>
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- Tests of fundamental forces of nature: $x < x_{K}$
- Electric dipole interactions: $x_{w} > x_{w} > x_{w} < x_{K}$
- Cold controlled chemistry: $x_{w} > x_{w} > x_{w} > x_{K}$
- Ultracold chemistry: $x_{w} > x_{w} > x_{w} > x_{K}$
- Quantum degeneracy with molecules: $x_{w} > x_{w} > x_{w} > x_{K}$
- Novel quantum phase transitions: $x_{w} > x_{w} > x_{w} > x_{K}$

Figure 1. The production of cold and ultracold molecules in different regions of spatial density $n$ and temperature $T$. Some technical approaches that are yet to be demonstrated in experiments can potentially address the important region of $n \sim x_{w}^{7} - x_{w}^{9} \text{ cm}^{-3}$ and $T \sim x_{mK} - x_{\mu K}$. The panel in the middle shows applications of cold and ultracold molecules to various scientific explorations with the required values of $n$ and $T$. The various bounds shown here are not meant to be strictly applied, but rather they serve as general guidelines for the technical requirements necessary for specific scientific topics.

TWO MAINSTREAMS IN COLD MOLECULE INDUSTRY

• Cool down a molecule
• Produce molecule from cold atoms

Association: Perform chemistry using very cold ingredients
HEAT INCREASES INTERACTION, BUT WE ARE GOING TO COOL EVERYTHING

Heat helps chemical reaction, because:

1. higher collision rate

2. higher kinetic energy to penetrate chemical energy barrier

Then, why shall we go cold?
WHAT AND WHY “ULTRACOLD”

• The ingredients (atoms) must be cold to have cold products (molecules).

• “Ultracold” → S wave scattering → enhance inelastic collision and chemical reaction. (increase by $10^3$) ↔ It contradicts with our experience in chemical practice.
The collision complex can be decomposed according to the angular momentum. s, p, d ...

During the process of the collision, the angular momentum must be conserved.

\[ \mathbf{L} = \mathbf{r} \times \mathbf{p} = 0 \]

\[ \rightarrow \mathbf{S} \]

\[ \rightarrow \mathbf{p} \]

Head-to-Head collision
**ULTRACOLD COLLISION**

Dipole-Dipole interaction

\[
v_d (\hat{r}) = \frac{\hat{D}_1 \cdot \hat{D}_2 - 3 \left( \hat{D}_1 \cdot \hat{r} \right) \left( \hat{D}_2 \cdot \hat{r} \right)}{r^3}
\]

Rank-2 Tensor: \( T^{(2)}q \)

Wavefunction of the complex during collision: \(|l,m>\)

The potential is: \( \langle l,m|T^{(2)}q|l,m> = 0 \)

\( l=0, \) s-wave scattering

dipole-dipole interaction is vanished
inelastic collision is enhanced
CROSS SECTION ENHANCEMENT

Head-to-Head collision
Averaged force is zero
No potential barrier
Furthermore, external field can be used to control the alignment, then the interaction of atoms

H$_2$ - Ar collision v.s temperature
OUR ULTIMATE GOAL: TO THE GROUND STATE
FROM COLD ATOMS TO COLD MOLECULES

• Energy conservation: How to remove internal energy?

• Vibration of neutral particles can not emit photons $\rightarrow$ no radiative decay!

• The third party is needed: photon or particle (three-body collision)
AVAILABLE APPROACHES

- Feshbach resonance: tuning interaction by external field, transfer kinetic energy to internal hyperfine (Adiabatic)

- Photoassociation: using photons to take out energy (Adiabatic or Not)
- Low rate, complicate laser system

- CW pumping low excitation rate

- Red detuned PA laser

- Spontaneous decay

- 4S+5P

- 4S+5S
A weakly bound system can increase PA rate. It was demonstrated that even absolute ground state near Fano–Feshbach resonance in the scattering state is reported in this focus issue [1]. In this focus issue, a pair of papers from the Côté group further expand the theoretical model of this 'Feshbach noptimized PA' hFOPAi process, discussing the possibility of reaching the unitarity limit for relatively small laser intensities and its application for producing ground state polar molecules [2].

The free–bound transition has strength similar to that of the simple PA scheme, but bound–bound transitions are greatly enhanced by the intermediate and short-range peaks from the strongly bound state contribution to the excited-state wave function. Here the coupling to small rates of bound molecule production enhances production of bound states from the two potentials – one is weakly bound but the other strongly bound. The free–bound transition has strength similar to that of the simple PA scheme, but bound–bound transitions are greatly enhanced by the intermediate and short-range peaks from the strongly bound state contribution to the excited-state wave function. Here the coupling to small rates of bound molecule production enhances production of bound states from the two potentials – one is weakly bound but the other strongly bound. The free–bound transition has strength similar to that of the simple PA scheme, but bound–bound transitions are greatly enhanced by the intermediate and short-range peaks from the strongly bound state contribution to the excited-state wave function. Here the coupling to small rates of bound molecule production enhances production of bound states from the two potentials – one is weakly bound but the other strongly bound.

The Franck–Condon overlaps are poor both for free–bound excitation and bound–bound decay, leading to small rates of bound molecule production. The FOPA method makes it possible to achieve large downward transition strengths for both the laser-driven upward transition and the spontaneous downward transition are determined primarily by Franck–Condon overlaps. The Franck–Condon overlaps are poor both for free–bound excitation and bound–bound decay, leading to small rates of bound molecule production. The FOPA method makes it possible to achieve large downward transition strengths for both the laser-driven upward transition and the spontaneous downward transition are determined primarily by Franck–Condon overlaps.
STIMULATED RAMAN ADIABATIC PASSAGE: STIRAP

\[ |A\rangle = (a_1 |1\rangle + a_2 |3\rangle)e^{i\alpha t} \text{ : coupled by laser 1} \]
\[ |B\rangle = (b_1 |2\rangle + b_2 |3\rangle)e^{i\beta t} \text{ : coupled by laser 2} \]

If laser 1,2 are \textit{coherent},

then \(|1\rangle\) and \(|2\rangle\) are coupled into a coherent dark state

\[ |\text{coherent dark state}\rangle = (r_1 |1\rangle + r_2 |2\rangle)e^{i\gamma t} \]

Population can be transferred between \(|1\rangle\) and \(|2\rangle\) with no access to \(|3\rangle\), therefore no spontaneous decay.
Apply external field to shift energy level and tune the interaction between atoms

\[ K + U_{\text{lowHF}} \rightarrow U_{\text{highHF}} \]

Free $\rightarrow$ Bound

The external fields can be:

- magnetic,
- optical,
- electrical

Figure 8. Creation of high-density ground-state polar molecules from dual-species ultracold atoms. The conversion process is fully coherent and preserves the phase space density of the original atomic gases in order to reach the quantum degenerate regime for the polar molecular gas. The colliding atom pairs from a near-degenerate dual-species atomic gas are converted to weakly bound Feshbach molecules by sweeping the magnetic field near an interspecies Fano–Feshbach resonance. This process allows the initial scattering state to be converted into a single bound level, albeit at a limited efficiency of about $\nu \rightarrow \nu_i$. In the second step, an optical Raman transfer scheme is employed to coherently transfer the weakly bound Feshbach molecules to the rovibration ground level of the electronic ground potentials. Rovibrational levels in the ground electronic state are first mapped out using coherent two-photon spectroscopy before implementing the actual state transfers. The actual population transfer is made via stimulated Raman adiabatic passage (STIRAP). The efficiency of the transfer process is shown to be above 99% and is crucial for maintaining the molecular phase space density. This high efficiency is enabled both by precise phase control of the pair of Raman optical fields via connection to a phase-stable optical frequency comb and by systematic spectroscopic studies of the relevant transition pathways for optimized transition strengths. In this focus issue, the use of wave packets is also discussed to aid the efficiency of a two-color conversion process, pointing out some important differences in the wave packet dynamics for heteronuclear and homonuclear molecules.

Recently, a spectacular series of papers have demonstrated highly efficient transfer to deeply bound levels using the STIRAP process based on a pair of CW lasers, including in an optical lattice in this focus issue. As shown in figure 8, the coherent transfer process takes two steps. First, atomic pairs are converted into loosely bound molecules using a Fano–Feshbach resonance. Then a coherent two-photon Raman process transfers the population from the initial, highly excited, molecular level to a much more deeply bound state. Thanks to good transition strengths, here it has been possible to transfer molecules to a variety of different states, including the $v = u$ level of the metastable $\alpha_{1}/\Sigma^1$ potential of Rb and KRb, and the absolute rovibronic ground state $X_{\nu}/\Sigma^1 (v = J = u)$ of KRb. The latter case...


Colliding atoms

\[ E_{\text{binding}} \]

molecules

Evidently, molecules

\[ R \]

Free

Bound

\[ r < R \]
THE BEST SOLUTION SO FAR

- Feshbach resonance + STRAP (stimulated Raman adiabatic passage)

- Form a very large (R, and high \( v \)) molecule, then remove vibrational energy by stimulation emission.

- CsRb and KRb have been successfully produced (Ni and et al, JILA, Science, 2008. Sage and et al, Yale, PRL, 2005)

Very classical, and low rate......
A PROPOSAL TO INCREASE PA RATE

• Can we drive population in all levels using one laser?  
  **A broad band laser!**

• Can we pump up population only, without stimulating it down?  
  **A pulse laser!**

⇒ **The femtosecond laser**
BANDWIDTH OF PUMP LASER

• The typical linewidth of molecular absorption without overlap with neighboring band →
  $\Delta \nu = 10^2$-$10^3$ cm$^{-1}$

• By uncertainty principle (Fourier transform-limited), $\tau =$ femtosecond
MAXIMUM INVERSION USING $\pi$

- Short pulse to perform $\pi$ population transfer.

- $\tau E_0 \mu / \hbar = \pi$

- Problems: very large $E_0 \sim 10^{12}-10^{14}$ W/cm$^2$. Many subtle effects should be taken into account, such as multi-photon transition
• $\tau E_0 \mu / \hbar = \pi$, a longer $\tau$ can lower required $E_0$

• To maintain the same $\Delta v$ with a long $\tau (> 1/\Delta v)$, we need a chirped pulse, rather than transform-limited.

*Longer pulse with the same power spectrum*
• The Blue Chirped pulse can remove energy (proposed by J. Cao et al, PRL 1998)

• just like Raman cooling
Coherent Control of Ultracold Molecule Dynamics in a Magneto-Optical Trap by Use of Chirped Femtosecond Laser Pulses

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The phase of the final products from each pulse is fixed, due to the coherent nature of comb laser.

\[ |\Phi\rangle_f = e^{i\theta}|\Phi\rangle + e^{i2\theta}|\Phi\rangle + e^{i3\theta}|\Phi\rangle \ldots \text{ interference of grating} \]

OUR APPROACH

- KRb mixture
- Polarization Gradient cooling
- Dipole trap
- FechBach resonance combination
- Photo-association (pulsed coherent Raman)
CHAPTER 3. Experiment Setup

In order to examine the quality of the alignment, we quickly turn off the magnetic field using the computer controlling program with the periodic time of 10 sec and look at the expanding cloudy. This could be a sign of the beam imbalance, poor alignment, or stray magnetic field. First, we adjust the current of the compensation coils to eliminate the stray magnetic field. And then, we align the reflected trapping beam to decrease the beam imbalance until the cloud expands uniformly in the optical molasses. While the MOT is collecting atoms, the gradient of the magnetic field must be set to optimize the number of atoms collected. We use 10 Gzcm in the axial direction.
K AND RB MIXTURE

\[ \frac{dN_K}{dt} = L - \gamma N_K - \beta n_K N_K - \beta' n_{Rb} N_K \]

\[ N_K = N_0 \{1 - \exp[-(\gamma + \beta n_K + \beta' n_{Rb})t]\} \]

\[ N_0 = \frac{L}{(\gamma + \beta n_{Rb} + \beta' n_K)} \]
A LITTLE BIT COLDER USING PG COOLING

Figure 3.39: Temperature measurement of the atomic cloud.

Figure 3.38: (a) The image sequence of the expansion cloud without polarization gradient cooling. (b) (c) The image sequence of the expansion cloud in the process of the polarization gradient cooling.
DIPOL TRAP FOR ULTRACOLD ATOM

Figure 4.10: Image taken of freely ballistic expansion in different release time in the dipole trap experiment.
CONCLUSIONS

• JILA experiment (KRb) is very **successful**, but the laser system of two cw lasers, one comb laser, and one ionization laser is very **complicate**.

• Direct comb driving PA is **attractive and promising**. Although, the oxford experiment discouraged. How to optimize pulse shape and spectrum is still **unclear**. There is a long way to go.