Chapter 17
Ultracold Molecules: Production and Application

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17.1 Introduction

First, I would like to introducet ultracold molecules. The motivation for studying ultracold molecules was nicely introduced in the previous chapter. I just would like to emphasize that a cold molecular gas is one of the biggest frontiers left for us [1]. Figure 17.1 shows my simplified view of the relevant fields. Imagine you want to do a precision measurement based on particles in the gas phase. Natural candidates are atoms, ions, and molecules. Cold atoms have been already produced by laser-cooling, and the properties of the ultracold atomic gas have also been well studied—as you know, these studies led to the Nobel Prize in Physics in 1997 and 2001. Cold ions have been laser-cooled before atoms were laser-cooled. The study on the interaction between cold ions enabled the manipulation of entangled states with ions, and the experimental study on cold-trapped ions led Dr. Wineland to receive a Nobel Prize in Physics (2012). Compared to these, there are not so many clear results on cold molecules: ultracold molecular gas is still in its infancy.

Cold molecules are difficult to make. One cannot use laser-cooling for producing ultracold molecules. Let me explain why by comparing atoms and molecules. Just by shining laser beams into a glass cell, one can cool atoms in the cell to 100 μK or less. This is possible because the same atom can scatter a lot of photons. For laser-cooling atoms to an ultracold temperature, one needs a large number of photon scatterings, since momentum transfer per one photon scattering is quite small. The common number of photon scattering needed to reach an ultracold temperature is on the order of 10,000 or more.

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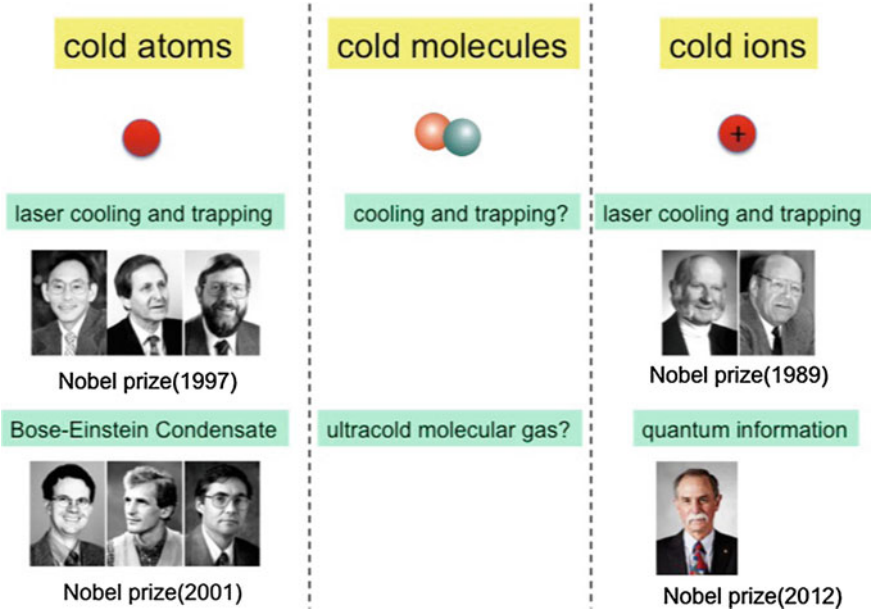

Fig. 17.1 Motivation behind studying ultracold molecules [2]

On the other hand, molecules do not scatter many photons. More precisely, molecules tend to go into different ground states after scattering one photon. Atoms and ions have only one electronic ground state. Therefore, after the photon scattering, they always move to the same ground state. However, molecules have a lot of rotational or vibrational degrees of freedom. Thus, after scattering one photon, molecules tend to go into different vibrational and rotational states. Once the molecules join other vibrational and rotational levels, they do not absorb the same laser light anymore. This is the reason why laser-cooling, which is a strong technique for cooling atoms and ions, does not work for molecules.

However, if you are dealing with simple molecules like diatomic molecules, there is a way around it: if one can develop a way to combine ultracold atoms into molecules without heating them up, then you should be able to produce ultracold molecules. This was the experiment we started ten years ago.

17.2 Preparation of Ultracold Molecules

How should we combine ultracold atoms into molecules? There is a special technique called "Feshbach resonance" [3]. Let me explain. Originally, "Feshbach resonance" was invented as a method to manipulate the interaction between ultracold atoms [4]. By applying an external magnetic field, one can bring another spin state into resonance, modifying the scattering process dramatically. This process was not only effective in modifying the amplitude of the scattering wave-function, but also enabled us to transform ultracold atoms into ultracold molecules. By just sweeping an external magnetic field, one can adiabatically transform the wave-function of atomic pairs into that of molecules.

However, molecules produced in this method have a serious drawback: they are fragile. Typical binding energies of those "Feshbach molecules" are only $\sim 10^{-8}$ eV, or 100 μK. Any type of interaction with the environment will either break up these molecules or induce vibrational quenching that transfers molecules into lower vibrational levels.

Our plan was to use light. We planned to use a two-photon transition to transfer loosely bound molecules into the ro-vibrational ground state. Once in their ground states, molecules are tightly bound, and they have a large electric-dipole moment. The molecules can interact with each other through dipole-dipole interaction, which is anisotropic and long range. This new type of interaction should allow us to explore physics in a wider range.

However, these two-photon transition are not easy to realize. In order to avoid heating, we cannot allow absorption of a single photon. Thus, the population is always hidden in the "dark state". This transferring process is based on mutual coherence between the two lasers and called "STimulated Raman Adiabatic Passage (STIRAP)". The necessary condition for realizing this process is to have large Rabi frequencies compared to laser line-widths and any other source of de-coherence. So this project requires lot of molecular spectroscopies to study the Franck Condon Factors, and lot of laser work to stabilize the laser line-widths. We used Resonance-Enhanced Multi-Photon Ionization (REMPI) to detect the molecules that went to the right rotational and vibrational levels.

After all the molecular spectroscopy, we found out that the best transition for STIRAP is the combination of 875 and 641 nm. We prepared light sources. We did not use a frequency comb, but instead we locked diode lasers to a highly stable cavity, which is made of Ultra Low Expansion (ULE) glass. The lasers were stabilized to kilohertz level. By just sweeping the intensities of those two laser beams, we have succeeded in transferring loosely bound molecules into tightly bound molecules [5] (Fig. 17.2).

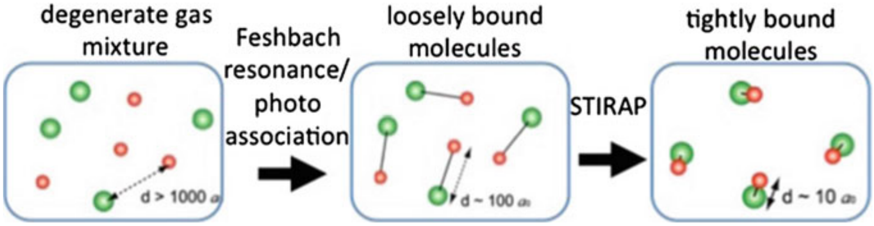

Fig. 17.2 How we produce ultracold molecules [5]

Here is a summary of the experiment for producing ultracold molecules: we start with Rubidium (Rb) and Potassium atoms in a vacuum chamber. Those atoms were laser-cooled and trapped in the magneto-optical-trap (MOT). We shine a cw-laser beam into the magneto-optical trap to photo-associate those atoms into loosely-bound KRb molecules. Here, we have to mention that, instead of Feshbach resonance, we used photo-association, because we could not suppress the inelastic loss at the Feshbach resonance. Due to this change, the density of the molecule was lower, and the temperature of the molecule was higher than we planned. However, the repetition rate of the experiment became higher. After that, the loosely bound molecules are converted into tightly bound molecules in the ro-vibrational ground state by STIRAP.

So now, we produced ultracold KRb molecules in the ro-vibrational ground state. Actually we can produce ultracold molecules in any rotational or vibrational level we want. Is there any advantage to producing ultracold molecules in a desired state? In the next experiment, we show that we can improve the accuracy of the measurement of the variation of fundamental constants by preparing molecules in a desired state. We succeeded in improving the world record by a factor of two [6].

17.3 Variation of Fundamental Constants

Let me explain the motivation for measuring the variation of fundamental constants. Currently, one of the biggest mysteries in physics is the accelerated expansion of the universe [7]. Although the observation of the accelerated expansion is established, there is a big controversy in understanding the origin. Especially, the source for energy needed to support the expansion is unknown. People named the energy "dark energy". The density of the "dark energy" is so low that it is quite difficult to detect the energy directly. There are so many theories on "dark energy". There are theories ("quintessence") that predict that the energy is stored in the form of fluctuations of a new scalar field [8]. The field can couple with other fields (e.g., the electromagnetic fields), causing fundamental constants to fluctuate. The fluctuation is expected to be of a low frequency.

Thus, it is very important to measure the fluctuation of fundamental constants. For this purpose, we can measure dimensionless fundamental constants like a fine-structure constant, electron-to-proton mass ratio, or proton g-factor. We decided to look into the electron-to-proton mass ratio.

There are two ways to look into the variation of fundamental constants. One is called "astronomical observations" where people investigate with an observatory and compare the spectra observed in the early universe with those measured in the laboratory. One of the astronomical observations based on microwave transition of alcohol shows that electron-to-proton mass ratio is stable at 10^{-7} in 7 billion years [9]. The other approach is to pursue the high-precision frequency metrology in the lab. You can measure the frequency of a molecular transition with better than 10^{-14} accuracy and compare the result with the one you obtained the day before.

The reason why molecular spectroscopy is needed for measuring the stability of electron-to-proton mass ratio is as follows. If you assume the Born-Oppenheimer approximation, the potential energy curve for a nucleus is determined by the electron mass and the fine-structure constant. If the properties of electron are stable, there is no chance for the potential-energy curve to change.

However, what we measure is the frequency caused by the motion of the nucleus, and that is sensitive to the mass of nucleus. Suppose that the electron mass stays the same, but the proton mass changes: Then, the vibrational frequency of the molecule changes because the frequency is inversely proportional to the square root of the mass of the nucleus. So by measuring the transition frequency between vibrational levels of molecules precisely, one can tell the stability of the electron-to-proton mass ratio.

Currently, the most precise lab measurement was done by a French group, who worked on the molecular spectroscopy of SF_6. They achieved a 5×10^{-14} level of accuracy by combining an optical spectroscopy of thermal SF_6 beam, a frequency comb, and an atomic clock [10]. Since the atomic clock sits in a different city ($\sim$40 km away), they had to use an optical-fiber link. What I would like to show you is that you can surpass this measurement by using ultracold molecules. The experiment can be contained on a single optical table. By using ultracold molecules, one can: (i) eliminate Doppler broadening, (ii) increase the interaction time, and (iii) eliminate signals from other transitions since one can prepare ultracold molecules in any target state.

Theoretical predictions showed that bi-alkali molecules have a microwave transition whose frequency is quite sensitive to electron-to-proton mass ratio. We scrutinized the molecular potential of KRb and found a good candidate: the fractional change in the frequency of this transition is about 14,890 times the fractional change in the electron-to-proton mass ratio. This is a huge gain compared to the experiments using thermal beams, where this factor is only on the order of one.

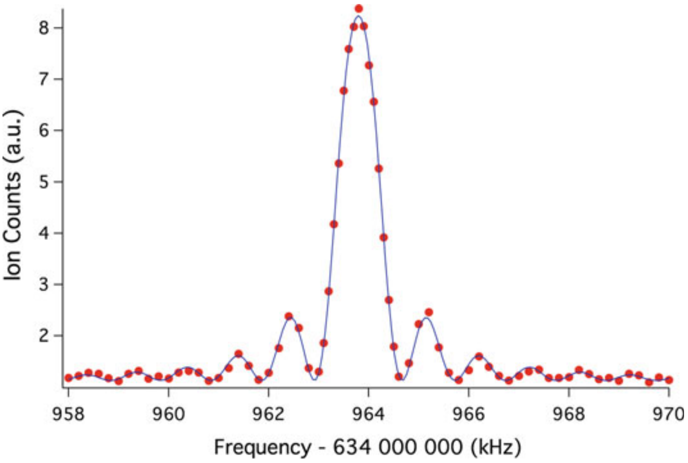

Fig. 17.3 Typical excitation spectra for measuring the stability of the electron-to-proton mass ratio [6]

In order to transfer ultracold molecules into this target state, we prepared another ULE cavity, locked two diode lasers for Raman transition. Using those two new laser beams, we succeeded in realizing STIRAP to the target state. We made an excitation spectra of the ultracold molecules, and measured the drift of the peak of the spectra over a year.

Even if the fundamental constants are stable, any fluctuations of experimental conditions can cause drifts in the spectra. Fluctuation of the magnetic field is one of them. In order to minimize the effect, we used a transition that does not have a linear Zeeman effect. Still there is a second-order Zeeman effect, but we also eliminated the effect from that by simultaneously taking excitation spectra of magnetic-field-sensitive microwave transitions and subtracting the second-order Zeeman shift from the measured peak frequencies.

As shown in Fig. 17.3, the result shows that the electron-to-proton mass ratio is constant within 2.8×10^{-14} [6]. This result is a factor of two improvement in accuracy over the previous world record.

The major part of the work has been done by Dr. Kobayashi and Mr. Ogino, who was a master course student.

References

1. L.D. Carr et al., New J. Phys. **11**, 055049 (2009)
2. Photos from Nobelprize.org
3. C. Cheng et al., Rev. Mod. Phys. **82**, 1225 (2010)
4. S. Inouye et al., Nature **392**, 151 (1998)
5. K. Aikawa et al., Phys. Rev. Lett. **105**, 203001 (2010)
6. J. Kobayashi et al., in preparation
7. P.J.E. Peebles, B. Ratra, Rev. Mod. Phys. **75**, 559 (2003)
8. E.J. Copeland, M. Sami, S. Tsujikawa, Int. J. Mod. Phys. D **15**, 1753 (2006)
9. J. Bagdonaite et al., Science **339**, 46 (2013)
10. A. Shelkovnikov et al., Phys. Rev. Lett. **100**, 150801 (2008)