

The photoassociation reaction of ultracold atoms

Yu Wang, and Qing-Tian Meng*

*School of Physics and Electronics, Shandong Normal University, Jinan, 250014,
the People's Republic of China*

Received 12 September 2015; Accepted (in revised version) 18 October 2015

Published Online 15 November 2015

Abstract. Photoassociation reaction is the process in which two colliding atoms (or the colliding atom-molecule system) absorb a photon to form an excited molecule. Since the researches based on the ultracold atomic and molecular systems have attracted great attention both from theorists and experimentalists, the ultracold photoassociation reaction is becoming an ascendant research field. In this paper, we review briefly the investigation history of the photoassociation reaction for ultracold atoms, especially the basic theory of collision and the photoassociation in different light fields, and the research on the external-field manipulation of ultracold atoms collisions is also prospected.

PACS: 34.10.+x, 34.50.Rk, 39.25.+k, 82.30.Nr

Key words: ultracold atoms, photoassociation reaction, collision theory.

1 Introduction

In recent decades, the development of laser techniques have made many new phenomena of laser-atom or laser-molecule interaction observed and investigated, such as ac-Stark shift [1,2], multiphoton ionization [3-7], laser-induced continuum structure [8-10], and photoassociation reaction [11-15], etc. In the investigation of photoassociation, it is found that the temperature of the samples is essential for the optical excitation and emission processes, i.e., the cold samples is beneficial to achieving the photoassociation spectroscopy with high resolution. In addition, the low temperature condition has other advantages that the formed production is more stable, and the reaction can be easily controlled by external fields, due to the translational energy of the system is very low. For the acquiring of low temperature, the laser-cooling technique is an alternative and the obtained temperature can be in the range from a few mK to several μK (ultracold). Another cooling technique is the so-called evaporative cooling, which has been reviewed by

*Corresponding author. *Email address:* qtmeng@sdsu.edu.cn (Q. -T. Meng)

W. Ketterle [16], E. A. Comell and C. E. Wieman [17]. It can be also used to cool atom to even lower temperatures in the quantum degenerate limit where atomic Bose-Einstein condensation (BEC) occurs [18].

The success of ultracold atom preparation on experiments stimulates and promotes the study of ultracold molecules. Because molecules have vibrational and rotational degree of freedom, and a possible magnetic dipole moment or electric dipole moment provides more possibilities for the manipulation of molecule, the study of productions and applications of cold molecules will be more challenging and pioneering. However, the production of ultracold molecules is of great significance for molecular matter waves [19], highly precise molecular spectrum [20], coherent molecular chemistry [21], quantum information processing [22,23] and so on, so it becomes a very important research topic of the atomic and molecular physics to seek effective methods of producing ultracold molecules. Fortunately the realization of ultracold atoms offers new ways for producing ultracold molecules. According to the ways they are obtained by associating ultracold atoms using external field, either optical field, or magnetic field, the associating scheme can be classified correspondingly into two kinds, i.e., magnetoassociation and photoassociation. Magnetoassociation is also called magnetic Feshbach resonance, in which the magnetic field is used to adjust the interatomic interactions, so that the two colliding atoms form a metastable molecules [24]. Photoassociation is the process in which two colliding atoms absorb a photon to form an excited molecule [25]. Compared with magnetic Feshbach resonance techniques, photoassociation has a lower requirement for ultracold atoms samples, and has the advantages of high efficiency, low energy levels and stable states when producing ultracold molecules. In Some literatures it is also called the optical Feshbach resonance [26].

Photoassociation has been studied both experimentally and theoretically. In 1987, the concept of photoassociation was first introduced by Thorsheim *et al.* [27] Since then, many ultracold diatomic molecules [28-40] have been associated using this technology, but with very low forming efficiency. In 1998, a new method was proposed to solve the above problem, which used stimulated Raman photoassociation technique to form ultracold molecules in alkali metal atomic BEC [41]. Four groups reported the photoassociative production of three different ultracold heteronuclear diatomic molecules in 2004 [37-39,42]. In 2011, Zhang Wei and Cong Shu-Lin *et al.* [43,44] investigated the photoassociation dynamics implemented by a series of asymmetric slowly turned-on and rapidly turned-off laser pulses, and in the same time they also demonstrated the photoassociation dynamics of ultracold cesium atoms being controlled by varying the corresponding parameter. In 2012, Lin Feng and Zhang Wei *et al.* [15] researched the dependence of photoassociation probability on the cut-off position of the laser pulse. In 2014, Jesús Pérez-Ríos *et al.* [45] have theoretically considered two photo-assisted collisional processes between ultracold particles namely between an atom and a molecule, or between molecules, in order to create ultracold trimers or tetramers. From the introduction presented above, we can see that the photoassociation technology has got great development. To help people understand it systematically, a review of it is necessary.

In this paper, we review briefly the study on photoassociation reaction of two colliding ultracold atoms. The remainder of this paper is organized as follows. Section 2 introduces the basic concepts of the collision theory. The important role of external field which plays in the study of the photoassociation reaction of ultracold atoms is given in Section 3. We look to the future in Section 4.

2 The collision theory in a light field

In the interaction of matters, collision is the most basic physical and chemical processes. Collision process can be influenced by collision energy, collision direction and the molecular internal state. The research on collision theory is important for us to understand the basic structure of material and the mechanism of chemical reaction. Particularly, low energy collision is essential for photoassociation due to its easily being controlled by external fields.

2.1 Scattering resonances

Scattering resonances play important roles in numerous collision processes occurring in atomic, nuclear, high-energy and cold atomic physics. Some resonances can be tuned by external fields. Tunable resonances can also be used to modify collisional properties, including the macroscopic properties of quantum degenerate gases.

The scattering resonance is generally classified as the shape resonance and the Feshbach resonance. In a shape resonance, the particle is temporarily trapped in a one-dimensional potential well by its own centrifugal barrier through which the particle will eventually escape by tunneling. The Feshbach resonance is a multichannel resonance due to the interaction of two or more states [46]. Rigorously speaking, the energy associated with the scattering coordinate is temporarily depleted through coupling to other degrees of freedom in a Feshbach resonance. As a result of collision resonances, the system is temporarily trapped and forms a quasibound or metastable complex.

Scattering resonances are significant for cold collision physics because they can be manipulated by external fields. Particularly, Photoassociation is an example of an optically-induced resonance.

2.2 Collisions in a light field

Much of the work on cold atomic collisions was carried out in a light field. Therefore, it is useful to provide an overview of some of the concepts that are used in understanding cold collisions in a light field [47]. Fig. 1 shows schematically the general features of a cold binary collision. The horizontal axis is the distance between two nuclei, and the vertical axis is the potential energy of the system.

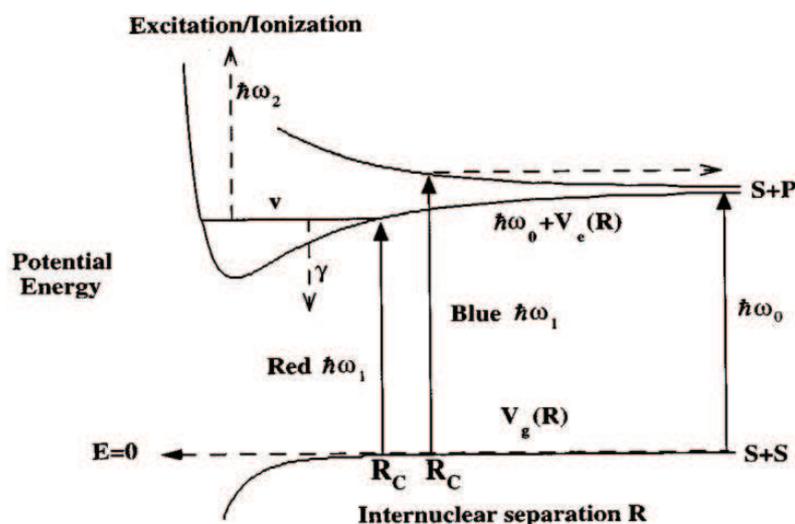


Figure 1: Schematic of a cold collision. Light field of red detuned excites the quasimolecule in a free-bound transition around the Condon point R_C , and causes excitation or ionization with the absorption of another field $\hbar\omega_2$.

Two S ground-state atoms interact at long distance through electrostatic dispersion forces, and close to each other along an attractive C_6/R^6 potential, then lead to a collision reaction. If the colliding atoms on the ground state are subject to an optical field $\hbar\omega_1$ which is less than $\hbar\omega_0$ (red-detuned), they will absorb the photon, and the probability of a free-bound transition to some vibration level v of the attractive excited state will maximize around the Condon point R_C . The excited-state molecule finds itself photoassociated and vibrating within the attractive well. The quasi-molecule will emit a photon γ to return to the ground state of free or bound state, or be further excited or even ionized by another field $\hbar\omega_2$. If the atoms colliding on the ground state potential encounter a optical field $\hbar\omega_1$ which is greater than $\hbar\omega_0$ (blue-detuned), the probability of transition to some continuum level of the repulsive excited state will maximize around the Condon point R_C . And blue-detuned excitation leads to optical shielding and suppression of inelastic and reactive collision rates.

3 The photoassociation reaction of ultracold atoms

Recent advances in the techniques of atomic manipulation with laser fields stimulates scientists to study the neutral molecules, even the cooling, trapping and manipulation of polar molecules. Ultracold molecules have attracted a lot of attentions from either theorists or experimentalists. People are looking forward to seeing more physical phenomena in cold molecular system.

Molecules with complex internal structure make them substantially harder to cool than atoms. Laser cooling is only applicable to a small fraction of atomic species where a

closed transition between two states exists. Since molecules generally have a much more complex level structure than atoms, including the multiple vibrational and rotational energy levels, it is therefore very difficult to find good transitions for cooling. In order to achieve this goal, many efforts have been put into it.

Generally, there are two different ways to produce a cold sample of molecules [48]: direct cooling of bound molecules and association of ultracold atoms (indirect cooling). Direct cooling techniques have been used to cool a series of large molecules, but the temperatures reached are in a range between a few mK and several K with these techniques. Due to the complicated structure of molecules, it is very hard to directly cool them down to a very low temperature. In contrast, indirect cooling techniques can associate two colliding atoms into a cold molecule using photoassociation [25] or magneto-association [24] after well-developed laser and evaporative cooling techniques are applied to cool the atoms. The technique of indirect cooling can produce a molecular sample with a temperature below one μK . So to obtain the samples with much lower temperature, the technique of indirect cooling is an attraction option. While magnetic coupling schemes require a Feshbach resonance at sufficiently low magnetic fields and allow only for the production of cold molecules in weakly bound states, optical coupling schemes are more universal [49]. From here on we just introduce the photoassociation detailedly.

3.1 Continuous-wave photoassociation

Continuous-wave (hereafter cw) photoassociation was first proposed by Thorsheim *et al.* [28]. During this process, two colliding ground-state ultracold atoms absorb a photon and form an electronically excited molecule:



Due to the Franck-Condon principle the photoassociation takes place at relatively large internuclear separations and usually, the excited state molecule will decay into two free atoms, reemitting another photon:



But occasionally the excited state molecule will decay to a bound ground state molecule:



To increase the probability for decaying into stable ground state molecules, we have to use excited states with good Franck-Condon factors for transitions to the ground state at small internuclear separations. This process has been successfully implemented to form a range of homonuclear [14] and heteronuclear [38,39,42] molecules in a magneto-optical trap.

Photoassociation has been demonstrated to be a widely applicable technique for producing cold molecules in a range of homonuclear and heteronuclear species [50]. However, the excited state molecules produced by one-photon photoassociation may form

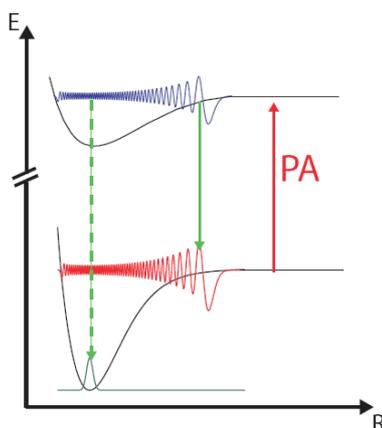


Figure 2: Continuous wave photoassociation. When a gas of atoms is illuminated with continuous laser (red arrow), two colliding atoms absorb a photon and photoassociate to form a bound excited-state molecule.

ground state molecules by spontaneous radiation (but the rovibrational energy levels cannot be chosen), or may decay into two free atoms. It is worthy to note that because of the nature of the association process, ultracold molecules are often formed in a high vibrational state. The strategies must be devised to produce translationally cold molecules in the desired vibrational state. To date the Stimulated Raman Adiabatic Passage (STIRAP) [51,52] is regarded as the most effective way to solve the above problems. For a more complete discussion, the reader is referred to the extensive literature on the STIRAP.

3.2 Ultrafast photoassociation

With the continuous development of laser technology, ultrafast laser pulses have been applied to the realization of the photoassociating, in which pulses with a spectral bandwidth of a few wave numbers were used, as shown in Fig. 3. It would allow for larger formation rates of excited state molecules, and improve the efficiency of photoassociation. This choice is motivated by the requirement of exciting a narrow band of transitions with large free-bound Franck-Condon factors close to the atomic resonance without exciting atomic transitions [53]. The main difference from cw excitation is as follows: several vibrational levels can be populated in the photoassociation step, and the pump pulse can be shaped in order to compensate for the dephasing of the wave packet and produce spatial focusing. These different exciting processes make it possible to increase the photoassociation rates.

However, it is necessary to control population in a low vibrational state to obtain the stable molecule because the excited state molecule is not stable, and decay easily into two free atoms. Recently, several promising theoretical schemes were proposed that use stimulated emission as the second step of the process [54]. This can be done via STIRAP or using chirped pulses [55] or by a repeated pump-dump process [56]. Note that the use

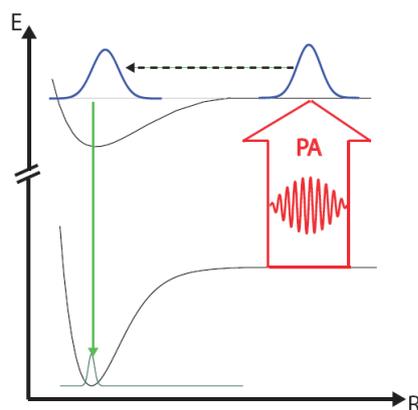


Figure 3: A schematic diagram of ultrafast photoassociation. When a gas of atoms is illuminated with an ultrafast laser pulse (red arrow), a larger formation rate of excited state molecules is obtained.

of ultrafast “pump” and “dump” pulses would permit the fully coherent transfer of population from free atom pairs to deeply bound vibrational states [57]. As a shorthand, we use the term “two-color photoassociation” to refer to the process in which one ultrafast laser pulse excites a wave packet in the electronically excited state, then a second shorter pulse dumps this wave packet to the electronic ground state. The first pulse is used to accelerate the wave packet in order to increase the number of particles into the reaction zone, a second pulse to increase the probability of photoassociation reaction. In fact, two-color photoassociation has been suggested in cw photoassociation, but such experiments are hardly feasible since the scheme is fully reversible, i.e., photodissociation will occur at the same time with the equal probability.

So far, it is still at the initial stage to detect and control atomic association reaction with ultrafast lasers because of a lot of challenges facing. Many scientists are developing more perfect methods to control the generation of ultracold molecules, and studying spectral characteristics of these molecules to control the chemical reaction more accurately.

4 Outlook

Above we have focused on the basic concept of collision and the PA in different light field. Besides, since the researches based on the ultracold atomic and molecular systems have attracted great attention both from theorists and experimentalists, most of them are spent in the unique role of the ultracold atomic collision in understanding the mechanism of chemical reaction. With the development of ultrafast laser technology, the study about external field manipulating ultracold atomic and molecular collision to generate the products in the direction of the expected will also make new progress. Ultracold atom could be used for the construction of a realistic quantum computer and atomic clock. Ultracold molecules offer new opportunities for creative applications [58-60] like fundamental studies of few-body dynamics in atomic and molecular physics [61], quantum simulation

of Hamiltonians describing many-body phenomena like low-temperature Fermi fluids or artificial gauge fields [62, 63], quantum information processing [22,23], or ultracold chemistry governed by quantum properties of the particles [64].

The potential of scientific advances based on ultracold technology is extremely large and thus far barely tapped. While the ultracold diatomic molecules have been studied extensively, some ultracold trimers and tetramers and their photoassociation are being studied theoretically [45], it is reasonable to expect the realization of the association for other ultracold polyatomic molecules in the future either theoretically or experimentally. On the other hand, researchers are only studying alkali-metal atoms and few alkaline-earth metal atoms so far, more meaningful work refers to look for appropriate ways to associate other atomic species. It is hoped that this review can provide a rough idea for the relevant theoretical and experimental studies.

Acknowledgments. This work is supported by the Natural Science Foundation of Shandong Province (Grant No. ZR2014AM022). Partial financial support from the Doctoral Program Foundation of Institutions of Higher Education of China (Grant No. 2012370411 0002) is also gratefully acknowledged.

References

- [1] Degenhardt C.; Stoehr H.; Sterr U.; Riehle F. *Phys. Rev. A* 2004, 70, 023414.
- [2] Degenhardt C.; Stoehr H.; Sterr U.; Riehle F. *Phys. Rev. A* 2004, 70, 023414.
- [3] Meng Q. T.; Yang G. H.; Sun H. L.; Han K. L.; Lou N. Q. *Phys. Rev. A* 2003, 67, 063202.
- [4] Liu C. H.; Meng Q. T.; Zhang Q. G. *Chem. Phys.* 2006, 326, 344-348.
- [5] Liu, C.H.; Meng, Q. T.; Zhang Q. G. *Sci. China Ser. B* 2006, 49, 214-218.
- [6] Zhang L. D.; Wei J.; Jiang Y. Y.; Fang L.; Zhang S. D.; Guo W. Y. *Chin. Phys.* 1998, 7, 271.
- [7] Niu D. W.; Li H. Y.; Luo X. L.; Liang F.; Cheng S.; Li A. L. *Chin. Phys.* 2006, 15, 1511.
- [8] Li G. X.; Huang G. M.; Peng J. S. *Acta Phys. Sin-Ov. Ed.* 1998, 7, 422.
- [9] Eramo R.; Cavalier S.; Fini L.; Matera M.; Dimauro L. F. *J. Phys. B* 1997, 30, 3789.
- [10] Faucher O.; Hertz E.; Lavorel B.; Chaux R.; Dreier T.; Berger H.; Charalambidis D. *J. Phys. B* 1999, 32, 4485.
- [11] Zhang C. Z.; Zheng B.; Wang J. *Chin. Phys. B* 2013, 22, 023401.
- [12] Zhang C. Z.; Zheng B.; Niu Y. Q. *Sci China-Phys. Mech. Astron.* 2014, 57, 1879-1884.
- [13] Sage J. M.; Sainis S.; Bergeman T.; DeMille D. *Phys. Rev. Lett.* 2005, 94, 203001.
- [14] Fioretti A.; Comparat D.; Crubellier A.; Dulieu O. ; Masnou-Seeuws F. ; Pillet P. *Phys. Rev. Lett.* 1998, 80, 4402.
- [15] Feng L.; Wei Z.; Yu Z. Z.; Cong S. L. *Chin. Phys. B* 2012, 21, 073203.
- [16] Davis K. B.; Mewes M. O.; Andrews M. R.; Van Druten N. J. Durfee D. S.; Kurn D. M.; Ketterle W. *Phys. Rev. Lett.* 1995, 75, 3969.
- [17] Anderson M. H.; Ensher J. R.; Matthews M. R.; Wieman C. E.; Cornell E. A. *Science* 1995, 269, 198.
- [18] Dalfovo F.; Giorgini S.; Pitaevskii L. P.; *Rev. Mod. Phys.* 1999, 71, 463.
- [19] Greiner M.; Regal C. A.; Jin D. S. *Natu.* 2003, 426, 537.
- [20] Bartenstein M.; Altmeyer A.; Riedl S. *Phys. Rev. Lett.* 2005, 94, 103201.
- [21] Abo-Shaer J. R.; Miller D. E.; Chin J. K. *Phys. Rev. Lett.* 2005, 94, 040405.

- [22] DeMille D.; Phys. Rev. Lett. 2002, 88, 067901.
- [23] Yelin S. F.; Kirby K.; Côté R. Phys. Rev. A 2006, 74, 050301.
- [24] Chin C.; Grimm R.; Julienne, P.; Tiesinga E. Rev. Mod. Phys. 2010, 82, 1225.
- [25] Jones K. M.; Tiesinga E.; Lett P. D. Rev. Mod. Phys. 2006, 78, 483.
- [26] Fatemi F. K.; Jones K. M.; Lett P. D. Phys. Rev. Lett. 2000, 85, 4462.
- [27] Thorsheim H. R.; Weiner J.; Julienne P. S. Phys. Rev. Lett. 1987, 58, 2420.
- [28] Mosk A. P.; Reynolds M. W.; Hijmans T. W. Phys. Rev. Lett. 1999, 82, 307.
- [29] Herschbach N.; Tol P. J. J.; Vassen W. Phys. Rev. Lett. 2000, 84, 1874.
- [30] McAlexander W. I.; Abraham E. R. I.; Ritchie N. W. M. Phys. Rev. Lett. 1995, 51, 871.
- [31] Blangé J. J.; Zijlstra J. M.; Amelink A. Phys. Rev. Lett. 1997, 78, 3089.
- [32] Nikolov A. N.; Ensher J. R.; Eyler E. E.; Wang H.; Stwalley W. C.; Gould P. L. Phys. Rev. Lett. 2000, 84, 246.
- [33] Zinner G.; Binnewies T.; Riehle F. Phys. Rev. Lett. 2000, 85, 2292.
- [34] Gabbanini C.; Fioretti A.; Lucchesini A. Phys. Rev. Lett. 2000, 84, 2814.
- [35] Takasu Y.; Komori K.; Honda K. Phys. Rev. Lett. 2004, 93, 123202.
- [36] Nagel S. B.; Mickelson P. G.; Saenz A. D. Phys. Rev. Lett. 2005, 94, 083004.
- [37] Haimberger C.; Kleinert J.; Bhattacharya M.; Bigelow N. P. Phys. Rev. A 2004, 70, 021402.
- [38] Mancini M. W.; Telles G. D.; Caires A. R. L.; Bagnato V. S.; Marcassa L. G. Phys. Rev. Lett. 2004, 92, 133203.
- [39] Kerman A. J.; Sage J. M.; Sainis S.; Bergeman T.; DeMille D. Phys. Rev. Lett. 2004, 92, 153001.
- [40] Staunum P.; Kraft S. D.; Lange J.; Wester R.; Weidemüller M. Phys. Rev. Lett. 2006, 96, 023201.
- [41] Mmond P. D.; Kheruntsyan K. V.; He H. Phys. Rev. Lett. 1998, 81, 3055.
- [42] Wang D.; Qi J.; Stone M. F.; Nikolayeva O.; Wang H.; Hattaway B.; Stwalley W. C. Phys. Rev. Lett. 2004, 93, 243005.
- [43] Zhang W.; Wang G. R.; Cong S. L.; Phys. Rev. A 2011, 83, 045401.
- [44] Zhang W.; Zhao Z. Y.; Xie T.; Wang G. R.; Huang Y.; Cong S. L. Phys. Rev. A 2011, 84, 053418.
- [45] Pérez-Ríos J.; Lepers M.; Vexiau R.; Bouloufa-Maafa N.; Dulieu O. J. Phys. Conf. Ser. 2014, 488, 012031.
- [46] Courteille P.; Freeland R. S.; Heinzen D. J.; Verhaar B. J. Phys. Rev. Lett. 1998, 81, 69.
- [47] Weiner J.; Bagnato V. S.; Zilio S. Rev. Mod. Phys. 1999, 71, 1.
- [48] Carr L. D.; DeMille D.; Kreams R. V.; Ye J. New J. Phys. 2009, 11, 055049.
- [49] Schlöder U.; Deuschle T.; Silber C. Phys. Rev. A 2003, 68, 051403.
- [50] England D. Oxford University 2011.
- [51] Bergmann K.; Theuer H.; Shore B. W. Rev. Mod. Phys. 1998, 70, 1003.
- [52] Javanainen J.; Mackie M. Phys. Rev. A 1998, 58, 789.
- [53] Merli A.; Eimer F.; Weise F. Phys. Rev. A 2009, 80, 063417.
- [54] Koch C. P.; Shapiro M. Chem. Rev. 2012, 112, 4928.
- [55] Luc-Koenig E.; Kosloff R.; Masnou-Seeuws F.; Vatasescu M. Phys. Rev. A 2004, 70, 033414.
- [56] Koch C. P.; Kosloff R.; Masnou-Seeuws F. Phys. Rev. A 2006, 73, 043409.
- [57] Koch C. P.; Luc-Koenig E.; Masnou-Seeuws F. Phys. Rev. A 2006, 73, 033408.
- [58] Carr L. D.; Ye J. New J. Phys. 2009, 11, 055009.
- [59] Dulieu O.; Gabbanini C. Rep. Prog. Phys. 2009, 72, 086401.
- [60] Jin D. S.; Ye J. Chem. Rev. 2012, 112, 4801.
- [61] Blume D. Rep. Prog. Phys. 2012, 72, 086401.
- [62] Dalibard J.; Nascimbène S.; Natu. Phys. 2012, 8, 276.
- [63] Galitski V.; Spielman I. B. Natu. 2013, 494, 49.
- [64] Kreams R. V. Phys. Chem. 2008, 10, 4079.