Formation of Ultracold Molecules

- Grant No. DE-FG02-05ER15734

- Report Number: DOE-UCONN-ER15734

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Abstract

Advances in our ability to slow down and cool atoms and molecules to ultracold temperatures have paved the way to a revolution in basic research on molecules. Ultracold molecules are sensitive of very weak interactions, even when separated by large distances, which allow studies of the effect of those interactions on the behavior of molecules. In this program, we have explored ways to form ultracold molecules starting from pairs of atoms that have already reached the ultracold regime. We devised methods that enhance the efficiency of ultracold molecule production, for example by tuning external magnetic fields and using appropriate laser excitations. We also investigates the properties of those ultracold molecules, especially their de-excitation into stable molecules. We studied the possibility of creating new classes of ultra-long range molecules, named macrodimers, thousand times more extended than regular molecules. Again, such objects are possible because ultra low temperatures prevent their breakup by collision. Finally, we carried out calculations on how chemical reactions are affected and modified at ultracold temperatures. Normally, reactions become less effective as the temperature decreases, but at ultracold temperatures, they can become very effective. We studied this counter-intuitive behavior for benchmark chemical reactions involving molecular hydrogen.

Final Report: Grant DE-FG02-05ER15734

Formation of Ultracold Molecules

Robin Côté

This grant supported research in basic atomic, molecular and optical physics related to the formation and properties of ultracold moleculess. The duration of the grant was the 10 year period from 8/2005 to 10/2015. Most of the support from the grant was used to pay salaries of the PI, postdocs, and graduate students, and travel to conferences and meetings; some funds were used for supplies and dissemination of results (*e.g.* through publications cost). The results were in the form of publications in peer reviewed journals. There were 37 peer reviewed publications over these 10 years with 5 of the publications in Physical Review Letters; all of the other articles were in respected peer reviewed journals (Physical Review A, New Journal of Physics, Journal of Physics B, Chemical Physics Letters ...).

Below, I give the Program Scope, and elaborate on the results of each grant period, labeled A, B, and C, respectively. I list the publications in each period as [A...], [B...], and [C...], and also describe the outreach/dissemination and training activities resulting from DOE funding.

Program Scope

The original aims of this Research Program were to identify efficient approaches to obtain ultracold molecules, and to understand their properties. This scope has evolved over the years to cover the effect of dressed interactions on molecular dynamics. We often needed to calculate the electronic properties (energy surfaces, dipole and transition moments, etc.), as well as the interaction of the molecules with their environment (*e.g.*, external fields).

1 Grant Period A: August 1st 2005 to July 31st 2008

This first period, Grant Period A, covers interconnected topics related to ultracold molecules on 1) Formation of alkali hydrides, 2) Rydberg-Rydberg interactions, 3) Evanescent-wave mirrors for molecules, and 4) Degenerate Fermi gases. We summarize below our findings in each of them, listing the manuscripts published.

1.1 Projects

• Formation of alkali hydrides

We explored the formation of alkali hydrides from one- and two-photon photoassociation. We found that the one-photon formation rate for LiH and NaH in their $X^1\Sigma^+$ ground electronic state is sizable in the upper ro-vibrational states $|v'', J = 1\rangle$; assuming conservative conditions, the rate coefficients are of the order 3×10^{-13} cm^3/s, leading to about 30,000 molecules per second [A1]. We also found that all of those molecules would populate a narrow distribution of J-states in the $v'' = 0$ vibrational level by spontaneous emission cascading (see Fig.1).

In the two-photon case, we calculated the formation rate of LiH into the $X^1\Sigma^+$ singlet ground state via the $B^1\Pi$ excited state, which has only three bound levels (in the $J = 1$ manifold) and a fairly good overlap with $X^1\Sigma^+$. We found rate coefficients about 1000 times larger than the corresponding single photon case [A2]. However, back-stimulation into the continuum limits these larger rates to values of single photon processes followed by spontaneous decay into the $X^1\Sigma^+$ state [A2].

• **Rydberg-Rydberg interactions**

We began working on Rydberg-Rydberg interactions to explain some spectral features observed in ^{85}Rb experiments. We calculated the long-range molecular potentials between two atoms in $70p$ in Hund's case (c). We included the effect of fine structure, and showed how the strong ℓ-mixing due to long-range Rydberg-Rydberg interactions can lead to resonances in excitation spectra. Such resonances were first reported in S.M. Farooqi *et al.*, Phys. Rev. Lett. **91** 183002 (2003), where single UV photon excitations from the $5s$ ground state occurred at energies corresponding to normally forbidden transitions or very far detuned from the atomic energies. We modeled a resonance correlated to the $69p_{3/2} + 71p_{3/2}$ asymptote by including the contribution of various symmetries (see Fig. 2): the lineshape is reproduced within the experimental uncertainties [A3].
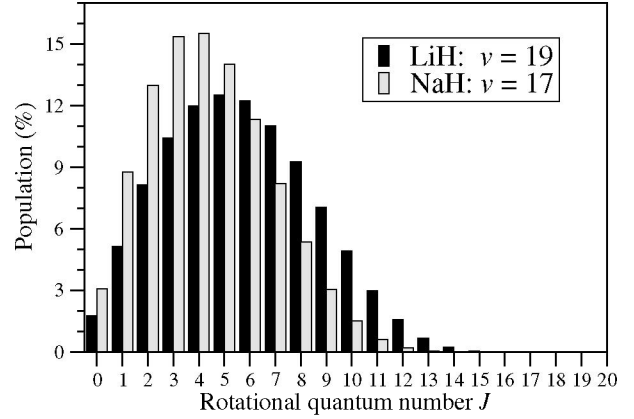

Figure 1: Distribution into the J states of the $v = 0$ manifold starting from $v = 19, J = 1$ for LiH and $v = 17, J = 1$ for NaH. In both cases, we observe that the maximum population is achieved around $J \sim 5$.
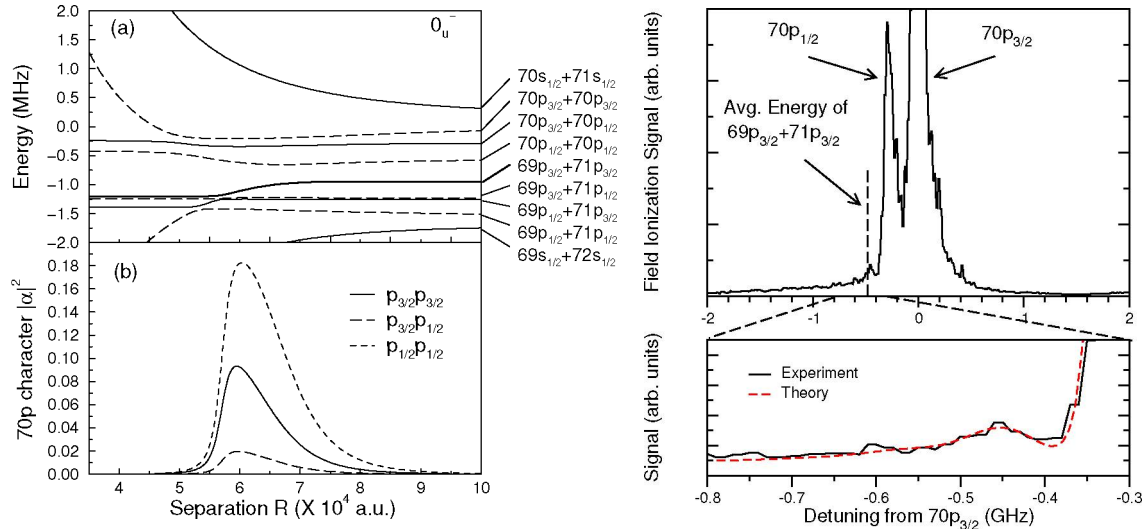

Figure 2: Left panel: (a) Potentials for the 0_u^- symmetry for asymptotes between $70s + 71s$ and $69s + 72s$ (zero of energy set at the $70p_{3/2} + 70p_{3/2}$ asymptote). (b) Fraction of $70p$ character $|\alpha|^2$ for $p_{3/2}p_{3/2}$, $p_{3/2}p_{1/2}$, and $p_{1/2}p_{1/2}$ mixtures of the $69p_{3/2} + 71p_{3/2}$ curve. Right panel: Experimental spectrum near the $70p$ atomic resonance. Zoom: comparison between experiment and theory (assuming a 120 MHz laser bandwidth, and contributions from the 0_g^+, 0_u^-, and 1_u symmetries).
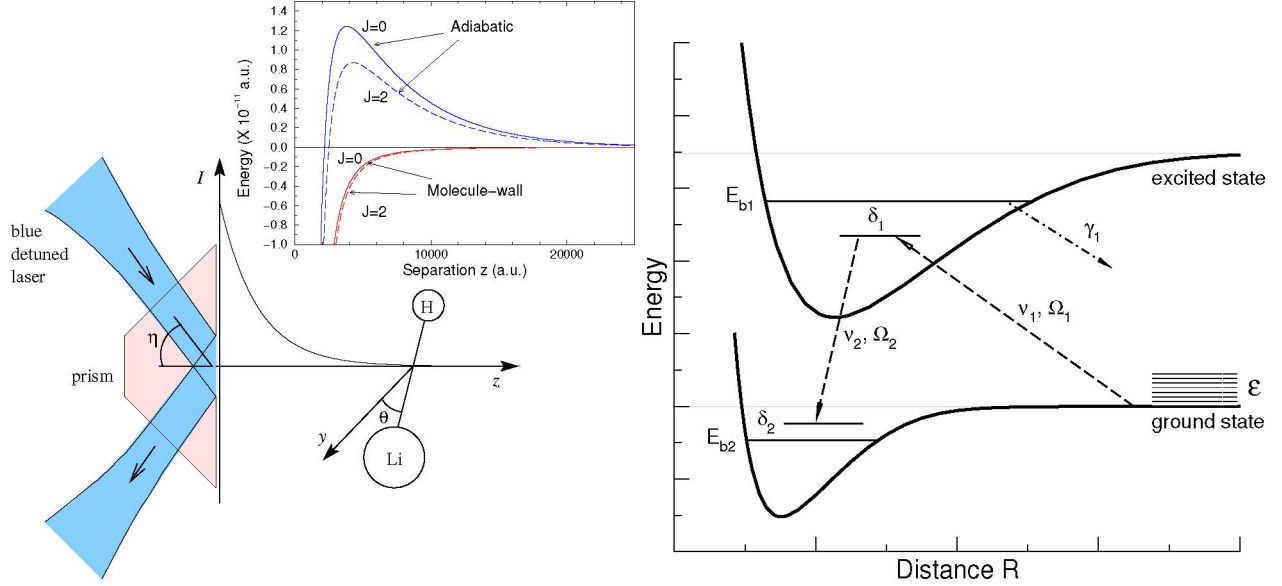
Figure 3: Left panel: Setup for a molecular EWM. Laser light enters a prism (index of refraction n, angle η) and undergoes total internal reflection. At a distance z outside the prism, the resulting exponentially decaying field interacts with the polar diatomic molecule. θ and ϕ are the angle between the molecular axis and the direction of the light polarization. *Inset*: Molecular-light and adiabatic potentials for $J = 0$ and 2. Right panel: Two-photon scheme, where the detunings are $\delta_1 = E_{b1} - h\nu_1 > 0$ and $\delta_2 = E_{b2} + h(\nu_2 - \nu_1) < 0$. The Raman probe scans the density of states of the colliding particles.

• Evanescent-wave mirrors

In [A4], we investigated the interaction of an ultracold diatomic polar molecule with an evanescent-wave mirror (EWM) (see Fig. 3, left panel). We found that the reflection/transmission coefficient depends on the internal (rovibrational) states of the molecules. Such molecular optics components could facilitate the manipulation and trapping of ultracold molecules, and might serve in future applications in several fields, *e.g.*, as devices to filter and select state for ultracold chemistry, to measure extremely low temperatures of molecules, or to manipulate states for quantum information processing.

• Degenerate Fermi gases

Quantum degenerate systems, such as Bose-Einstein condensates or degenerate Fermi gases, are being explored actively by numerous theoretical and experimental groups. In our initial work on Fermi gases, we focused on a two-photon probe to determine the temperature of the sample [A5]. In such a two-photon process (see Fig. 3, right panel), one can show that, as a function of the relative kinetic energy ε, the scattering matrix $|S(\varepsilon)|^2$ increases rapidly from zero at $\varepsilon = 0$ to reach a maximum value and drop sharply to zero for $\varepsilon = \delta_2$. Such sharp variations can be used to probe the density of states as a function of the relative collision energy [A5]. However, we showed that the relative velocity distribution g_{12} is quite different from the single-particle Fermi-Dirac distribution g: the Pauli exclusion principle prevents the distribution to become as narrow as the equivalent Maxwell-Boltzmann distribution as the temperature T is lowered below the Fermi temperature $T_F = E_F/k_B$. By averaging over this distribution and scanning δ_2, we predicted lineshapes that would reveal properties of the degenerate Fermi gas, such as the spectroscopic signature of Cooper pairs in ^{6}Li.

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1.2 Publications sponsored by DOE during Period A

A1. E. Juarros, P. Pellegrini, K. Kirby, and R. Côté, *One-photon-assisted formation of ultracold polar molecules.* Phys. Rev. A **73**, 041403(R) (2006).

A2. E. Juarros, K. Kirby, and R. Côté, *Laser-assisted Ultracold Lithium-hydride Molecule Formation: Stimulated vs. Spontaneous Emission.* J. Phys. B **39**, S965 (2006).

A3. J. Stanojevic, R. Côté, D. Tong, S.M. Farooqi, E.E. Eyler, and P.L. Gould, *Long-range Rydberg-Rydberg interactions and molecular resonances.* Eur. Phys. J. D **40**, 3 (2006).

A4. K. Shimshon, B. Segev, and R. Côté, *Evanescent-Wave Mirror for Ultracold Diatomic Polar Molecules.* Phys. Rev. Lett. **95**, 163005 (2005).

A5. M. Koštrun and R. Côté, *Two-color spectroscopy of fermions in mean-field BCS-BEC crossover theory.* Phys. Rev. A **73**, 041607(R) (2006).

1.3 Outreach/dissemination activities and Training

Research based on DOE support during Grant Period A was presented by the PI in a total of 6 invited talks at conferences and workshops (including 1 lecture at a Winter School in Les Houches), 5 invited talks at universities, and 6 contributed talks/posters (with students/ postdocs/colleagues) at conferences.

Four Ph.D. students have worked on projects described above: two of them have obtained their Ph.D. (Elizabeth Juarros: Ph.D. 07, and Jovica Stanojevic: Ph.D. 07), and two were in the middle of their projects (Ionel Simbotin and Marko Gacesa). J. Stanojevic was on the short list for the ITAMP Postdoctoral Fellowship, and he continued his career at the MPI in Dresden. E. Juarros took a maternity break after her graduation, and went for a postdoc in Edinburgh. In addition, one postdoctoral researcher (Dr. Philippe Pellegrini) has been directly involved in this work.

2 Grant Period B: August 1$^{\text{st}}$ 2008 to October 31$^{\text{st}}$ 2011

This second period, Grant Period B, covers interconnected topics related to ultracold molecules on 1) Formation of homonuclear and heteronuclear molecules, 2) Rydberg-Rydberg interactions, 3) Feshbach Optimized Photoassociation (FOPA), and 4) Energy surfaces and reactions. We summarize below our findings in each of them, listing the manuscripts published.

2.1 Projects

• Formation of homonuclear and heteronuclear molecules

In two previous papers sponsored by DOE [A1,A2], we explored the formation of LiH and NaH in their $X^1\Sigma^+$ ground electronic state from one- and two-photon photoassociative processes. We extended this work to the formation of LiH molecules in the $a^3\Sigma^+$ electronic state [B1]. It is predicted to support one ro-vibrational level, leading to a sample in a pure single ro-vibrational state. We found that very large rate coefficients ca be obtained by using the $b^3\Pi$ excited state, which supports only seven bound levels. Because of the extreme

spatial extension of their last "lobe", the wave functions of the two uppermost bound levels have large overlap with the ($v = 0, J = 0$) bound level of a$^3\Sigma^+$, leading to branching ratios ranging from 1% to 90%. This property implies that large amounts of LiH molecules could be produced in a single quantum state, a prerequisite to study degenerate molecular gases [B1]. In this work, we also discuss the implication of the statistics of the components of LiH (fermions or bosons) on the chemical reaction rates when colliding with H, Li, or LiH.

We also extended our earlier studies of PA in ^{86}Sr and ^{88}Sr atoms [S.B. Nagel *et al.*, Phys. Rev. Lett **94**, 083004 (2005);. P.G. Mickelson *et al.*, Phys. Rev. Lett **95**, 223002 (2005)], where we computed PA-rates and adjusted the potentials to reproduce the experimental data of Killian's group at Rice University (see Fig. 4) and to obtain the scattering length of both isotopes. We also analyzed results from two-photon photoassociative spectroscopy of the least-bound vibrational level ($v = 62$) of the X$^1\Sigma_g^+$ state of the ^{88}Sr$_2$ dimer [B2]. By combining measurements of the binding energy with an accurate short range potential and calculated van der Waals coefficients, we were able to determine the *s*-wave scattering length $a_{88} = -1.46a_0$. We also modeled the observed Autler-Townes resonance splittings. Through mass scaling, we determined the scattering lengths for all other isotopic

Figure 4: PA-rate for ^{86}Sr. The theoretical curve agrees well with the experimental data.

combinations. These measurements provide confirmation of atomic structure calculations for alkaline-earth atoms, and valuable input for experiments with ultracold strontium.

We suggested and analyzed a technique for efficient and robust creation of dense ultracold molecular ensembles in their ground rovibrational state [B3]; a molecule is brought to the ground state through a series of intermediate vibrational states via a multistate chainwise stimulated Raman adiabatic passage technique. We studied the influence of the intermediate states decay on the transfer process and suggested an approach that minimizes the population of these states, resulting in a maximal transfer efficiency. As an example, we analyzed the formation of ^{87}Rb$_2$ starting from an initial Feshbach molecular state and taking into account major decay mechanisms due to inelastic atom-molecule and molecule-molecule collisions. Numerical analysis suggests a transfer efficiency > 90%, even in the presence of strong collisional relaxation as are present in a high density atomic gas.

● **Rydberg-Rydberg interactions**

We extended our previous work Rydberg-Rydberg interactions explaining spectral features observed in ^{85}Rb experiments, namely a resonance correlated to the $69p_{3/2} + 71p_{3/2}$ asymptote [A3], to the case of strong resonances near the $69d + 70s$ asymptote [B4] when exciting $70p$ atoms. We found that such resonances are again attributed to strong ℓ-mixing. In this particular case, the resonances occur at energies corresponding to excited atom pairs
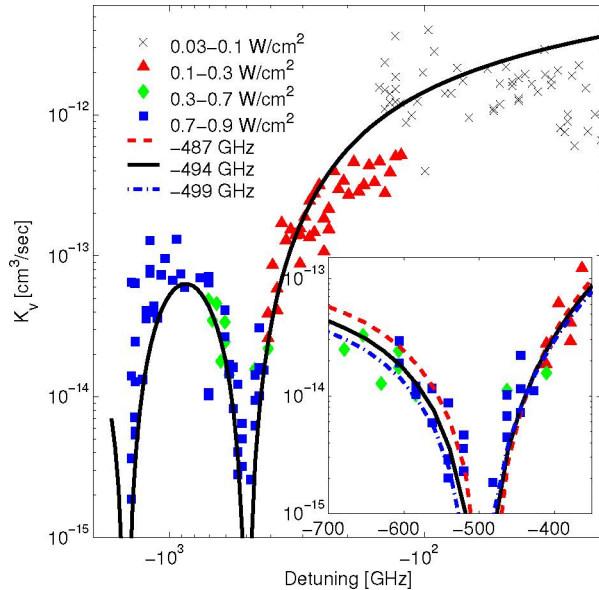
$(n-1)d + ns$. We also obtained the n-scaling of both the position and size of the resonances, n^{-3} and $n^{8.5}$, respectively. Our results (Fig. 5) agree well with measurements.

In [B5, B6], we investigate the interaction between two rubidium atoms in highly excited Rydberg states, and show the existence of potential wells for 0_g^+ symmetry of doubly-excited atoms due to ℓ-mixing. These wells are shown to be robust against small electric fields, and to support many bound states. We calculated their predissociation and show that their lifetimes are limited by the lifetime of the Rydberg atoms themselves. We also study how these vibrational levels could be populated via photoassociation, and how the signature of the ad-mixing of various ℓ-character producing the potential wells becomes apparent in photoassociation spectra.

Figure 5: Comparison of theoretical and experimental signals.

• Feshbach Optimized Photoassociation (FOPA)

We investigated the formation of polar molecules using photoassociation (PA) of atoms in mixtures in the vicinity of Feshbach resonances [B7]. We focused our attention on heteronuclear dimers for which the presence of a permanent dipole moment allows transitions from the continuum directly to a rovibrational level v of the ground electronic molecular states. The corresponding photoassociation rate coefficient $K_{PA}^v = \langle v_{\text{rel}} \sigma_{PA}^v \rangle$ depends on v_{rel}, the relative velocity of the colliding pair, and on σ_{PA}^v, the PA cross section. The bracket stands for an average over the distribution of v_{rel}: for heteronuclear systems, it is a Maxwell-Boltzmann distribution characterized by the temperature T.

We calculated the rate coefficients to form singlet molecules of LiNa using this Feshbach Optimized Photoassociation (FOPA) mechanism. To do so, we adapted our computer codes to not only calculate the scattering problem with all hyperfine couplings in a magnetic field, but also to give the wave functions for all channels, and their projection on the singlet electronic state $X^1\Sigma^+$. We found that the rate coefficients increase by 10^{3-4} when compared to the off-resonance rate coefficients (see Fig. 6). We also gave a simple analytical expression based on a two-channel model relating the rate coefficient to the off-resonance rate coefficient and parameters of the resonance (such as its position and width); the model reproduces very well the results of our fully-coupled numerical problem.
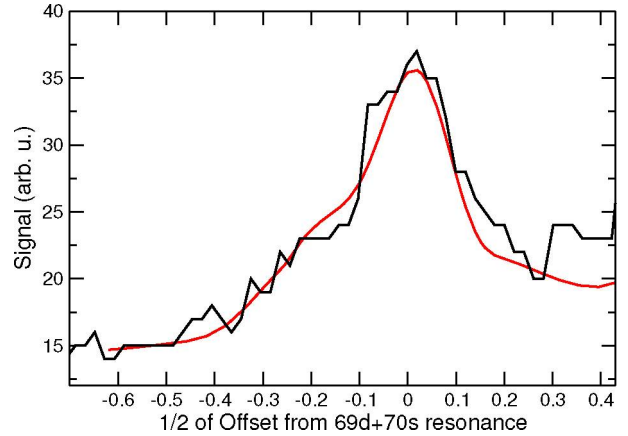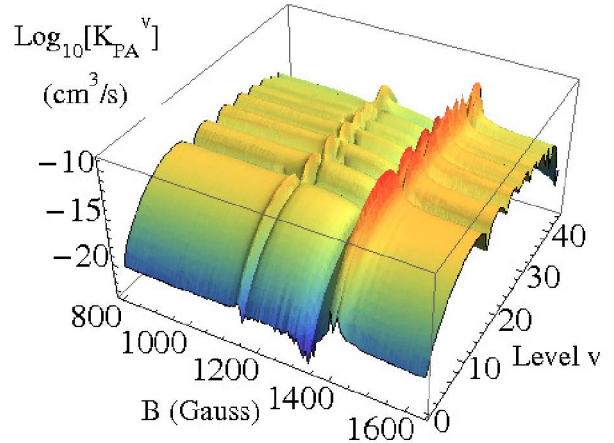

Figure 6: K_{PA}^v in cm^3/s vs. the B-field ($T = 120$ μK, $I = 1$ W/cm^2) for various levels $(v, J = 1)$ of the LiNa $X^1\Sigma^+$ potential, starting from ^{6}Li($f = \frac{1}{2}, m = \frac{1}{2}$) and ^{23}Na($f = 1, m = 1$). Two Feshbach resonances at 1142 and 1418 Gauss enhance the PA rates by several orders of magnitude.

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We expanded this work to take into account the effect of saturation on the rate coefficient [B8]. We computed rate coefficients and showed that new double-minima features would appear at large laser intensity near the resonance. We compared our theoretical results with recent experimental measurements on ^{7}Li obtained by Hulet and co-workers at Rice University, and found a good agreement without any adjustable parameters.

We combined this idea of FOPA with our previous work using STIRAP [B9]. We showed that it is possible to enhance the Rabi frequency between the continuum and an intermediate state so that the efficient transfer of a pair of atoms directly from the continuum into the ro-vibrational ground state becomes achievable with moderate laser intensities and pulse durations. This approach opens interesting perspectives, since it does not require degenerate gases to work efficiently.

Finally, we also explored the role of Feshbach resonance and spin-orbit coupling in the formation of ultracold LiCs molecules [B10]. We analyzed the experimental data of our co-workers, and found that even in the case of unpolarized atomic spin states (*i.e.* a mixture of all m_f states), hyperfine coupling can modify the formation rate measurably.

- **Energy surfaces and reactions**

In an effort towards reactive scattering involving cold molecules and molecular ions has started with the calculation of potential energy surfaces (PES) for trimers, such as for Li_3, where we study an energy surface necessary in the photoassociation of Li_2 with Li to form the Li_3 trimer. For example, we obtained PES for the lowest doublet electronic state of Li_3 ($1^2A'$) [B11], using the valence electron FCI method with atomic cores represented using an effective core potential, and investigated the Jahn-Teller splitting of the $1^2E'$ surface into the 1^2A_1 and 1^2B_2 states. We also calculated the lowest $^2A''$ surface arising from the $Li_2[X^1\Sigma_g^+]+Li^*[^2P]$ interaction [B12]. We also analyzed the long range behavior of this surface by fitting the *ab initio* calculations at long range with a functional series of the form $-C_n/R^n$.

Together with my collaborators, we have studied the collisions of trapped molecules with slow beams, particularly of OH($J = 3/2, MJ = 3/2, f$) molecules with ^{4}He atoms [B13]. We found that the calculated cross sections are consistent with recent experimental observations at low beam energies, and demonstrated the importance of including the effects of non-uniform trapping fields in theoretical simulations of cold collision experiments with trapped molecules and slow atomic beams. We also computed the various scattering processes in a benchmark system, namely H_2+D [B14], and found that both reaction and quenching rates depend strongly on the initial ro-vibrational state of H_2.

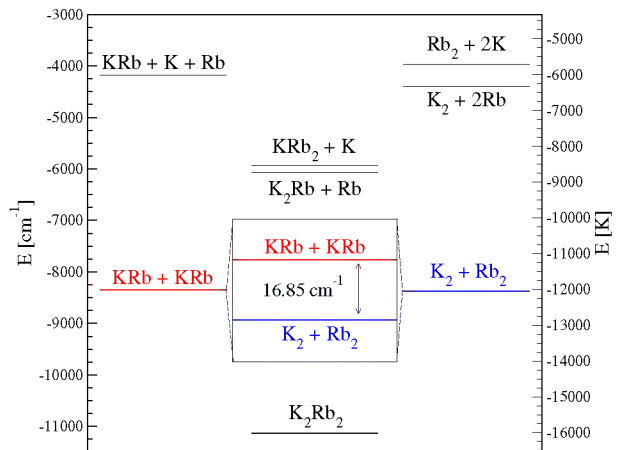

Figure 7: Diagram for fragment and structure energies involving KRb with KRb and separated atoms. Inset shows the small difference between the KRb + KRb and K_2 + Rb_2 asymptotes.

We also calculated the structure and thermochemistry relevant to KRb+KRb collisions and reactions [B15]. We found that the K_2Rb

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and KRb$_2$ trimers have global minima at higher energies than KRb+KRb, preventing the formation of those trimers by collisions. We also calcualted the energy minima for the tetramer K$_2$Rb$_2$ and found it to have two stable planar structures. We have calculated the minimum energy reaction path for the reaction KRb+KRb to K$_2$+Rb$_2$ and found it to be barrierless.

Finally, we started a new effort on molecular ions. In order to study their formation, we carefully calculate their energy surface and transition dipole moments. We started with alkaline-earth elements, since they can be cool to very low temperatures. In [B16], we report *ab initio* calculations of the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of the Be$_2^+$ dimer. We found two local minima, separated by a large barrier, for the $B^2\Sigma_g^+$: we computed the spectroscopic constants and found good agreement with the recent measurements. We also calculated bound vibrational levels, transition moments and lifetimes in this state.

2.2 Publications sponsored by DOE during Period B

B1. E. Juarros, K. Kirby, and R. Côté, *Formation of ultracold molecules in a single pure state: LiH in $a^3\Sigma^+$*. Phys. Rev. A **81**, 060704 (2010).

B2. Y.N. Martinez de Escobar, P.G. Mickelson, P. Pellegrini, S.B. Nagel, A. Traverso, M. Yan, R. Côté, and T.C. Killian, *Two-photon photoassociative spectroscopy of ultracold ^{88}Sr*. Phys. Rev. A **78**, 062708 (2008).

B3. E. Kuznetsova, P. Pellegrini, R. Côté, M.D. Lukin, and S.F. Yelin, *Formation of deeply bound molecules via adiabatic passage*. Phys. Rev. A **78**, 021402(R) (2008).

B4. J. Stanojevic, R. Côté, D. Tong, S.M. Farooqi, E.E. Eyler, and P.L. Gould, *Long-range potentials and $(n-1)d + ns$ molecular resonances in an ultracold Rydberg gas*. Phys. Rev. A **78**, 052709 (2008).

B5. N. Samboy, J. Stanojevic, and R. Côté, *Formation and properties of Rydberg macrodimers*, Phys. Rev. A **83**, 050501(R) (2011).

B6. N. Samboy and R. R. Côté, *Rubidium Rydberg macrodimers*, J. Phys. B **44**, 184006 (2011).

B7. P. Pellegrini,, M. Gacesa, and R. Côté, *Giant formation rates of ultracold molecules via Feshbach Optimized Photoassociation*. Phys. Rev. Lett. **101**, 053201 (2008).

B8. P. Pellegrini, and R. Côté, *Probing the unitarity limit at low laser intensities*. New J. Phys. **11**, 055047 (2009).

B9. E. Kuznetsova, M. Gacesa, P. Pellegrini, S.F. Yelin, and R. Côté, *Efficient formation of ground state ultracold molecules via STIRAP from the continuum at a Feshbach resonance*. New J. Phys. **11**, 055028 (2009).

B10. J. Deiglmayr, A. Grochola, M. Repp, R. Wester, M. Weidemüller, O. Dulieu, P. Pellegrini, and R. Côté, *Influence of a Feshbach resonance on the photoassociation of LiCs*. New J. Phys. **11**, 055034 (2009).

B11. J.N. Byrd, J.A. Montgomery (Jr.), H.H. Michels, and and R. Côté, *Potential energy surface of the $1^2A'$ Li_2+Li doublet ground state*, Int. J. of Quantum Chem., **109**, 3112 (2009).

B12. J.N. Byrd, J.A. Montgomery (Jr.), H.H. Michels, and R. Côté, *Electronic Structure of the Li_2 $[X^1\Sigma_g^+] + LI^*[P_2]$ Excited A'' Surface*, Int. J. of Quantum Chem **109**, 3626 (2009).

B13. T. V. Tscherbul, Z. Pavlovic, H. R. Sadeghpour, R. Côté, and A. Dalgarno, *Collisions of trapped molecules with slow beams*, Phys. Rev. A **82**, 022704 (2010).

B14. I. Simbotin, S. Ghosal, and R. Côté, *A case study in ultracold reactive scattering: D + H_2*, Phys. Chem. Chem. Phys. 13, 19148 (2011).

B15. J.N. Byrd, J.A. Montgomery (Jr.), and R. Côté, *Structure and thermochemistry of K_2Rb, KRb_2 and K_2Rb_2*, Phys. Rev. A 82, 010502 (2010).

B16. S. Banerjee, J. N. Byrd, R. Côté, H. H. Michels, J. A. Montgomery, Jr. *Ab initio potential curves for the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of the Be_2^+: Existence of a double minimum*, Chem. Phys. Lett. **496**, 208 (2010).

2.3   Outreach/dissemination activities and Training

Research based on DOE support during Grant Period B was presented by the PI in a total of 7 invited talks at conferences and workshops (including 1 lecture at the 2009 DAMOP Graduate Student Symposium), 8 invited talks at universities, and 14 contributed talks/posters (with students/postdocs/colleagues) at conferences.

Four Ph.D. students have worked on projects described above: two have obtained their Ph.D. (Marko Gacesa: Ph.D. 10, and Nolan Samboy: Ph.D. 11), and two were in the middle of their projects (Ionel Simbotin and Jason Byrd). Former student J. Stanojevic, after two years at the MPI in Dresden, continued his career at the Institut d'Optique in Palaiseau. Former student E. Juarros went into teaching at the Luna Community College, in Las Vegas (NM). Marko Gacesa became a postdoctoral fellow at the Smithsonian Center for Astrophysics. In addition, two postdoctoral researchers have been directly involved in this work: Dr. Philippe Pellegrini (now in France) and Dr. Subhas Ghosal.

3   Grant Period C: Nov. 1ˢᵗ 2011 to Oct. 31ˢᵗ 2015

This third and last period, Grant Period C, covers interconnected topics related to ultracold molecules on 1) Structure calculations, molecular properties, and reactions, 2) Intermolecular long-range interactions, 3) Dressed and Rydberg states, and 4) Formation of molecules. We summarize below our findings in each of them, listing the manuscripts published.

3.1   Projects

• Structure calculations, molecular properties, and reactions

A continuing effort of our group involved calculations of potential energy surfaces (PESs). We expanded our work on the $1^2A'$ [B11] and $^2A''$ [B12] PESs of Li_3, to *ab initio* calculations of the long-range PES of its ground state X^2A', including van der Waals coefficients and three-body dispersion damping terms for the atom-diatomic dissociation limit [C1]. We extended our work on K_2Rb_2 relevant to KRb+KRb scattering [B15] to all alkali tetramers formed from $X_2+X_2 \rightarrow X_4$, $X_2+Y_2 \rightarrow X_2Y_2$, and $XY+XY \rightarrow X_2Y_2$ association reactions [C2],

and found two stable tetramer structures, rhombic (D_{2h}) and planar (C_s), with barrier-less pathways for dimer association reactions.

Building on our experience on atom-molecule scattering, *e.g*, in non-reactive OH+He [B13] or reactive D + H$_2$ [B14] systems, we investigated resonances near the scattering threshold in the reactive benchmark system H$_2$+Cl [C3]. We found that the inelastic cross section scales as k^{-3} in the s-wave regime, due to the proximity of a pole in the complex k-plane. We extended the study to H$_2$+F and gave an explanation based on the properties of the Jost function in [C4]. We also explored the effect of nuclear spin symmetry in reactions of D with para/ortho-H$_2$ [C5], comparing our quantum calculations with a statistical model.

Finally, we kept working on molecular ions: in [B16], we reported *ab initio* calculations of the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of Be$_2^+$, and predicting two local minima separated by a large barrier in $B^2\Sigma_g^+$. We extended this work to Ca$_2^+$ in [C6], again finding a double-well in $B^2\Sigma_g^+$. We also helped analyze experimental results in reactions involving Na and Ca$^+$ [C7]. We recently computed the surfaces for RbOH$^-$ and RbOH [C8] to model the associative detachment reaction Rb+OH$^-(v,j)$ →RbOH+e$^-$, paying special attention to the angular dependence of the PES (Fig. 8). We found the rate to strongly vary with the ro-vibrational state of OH$^-$ due to a curve-crossing at short-range, pointing to an interesting inter-dependence of the electronic and nuclear motion.
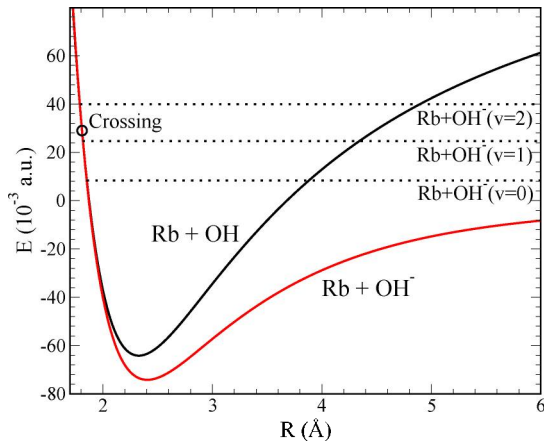

Figure 8: PES of Rb+OH and its anion computed along the $C_{\infty v}$ axis at the CCSD(T)/CBS level of theory. Also shown are the energy asymptotes for various OH$^-$ vibrational levels.

• Inter-molecular long-range interactions

In our previous work on K$_2$Rb$_2$ [B15], we calculated the minimum energy path for the reaction KRb+KRb→K$_2$+Rb$_2$ and found it to be barrierless. However, we recently showed that long-range barriers originating from the anisotropic interaction due to higher electrostatic, induction, and dispersion contributions could exist and stabilize a molecular sample [C9]. In addition, we showed that by changing the orientation of the molecules using an external DC electric field, and by varying its strength F, one could control the effective intermolecular interaction (Fig. 9). We generalized our treatment to the long-range interaction between homonuclear alkali
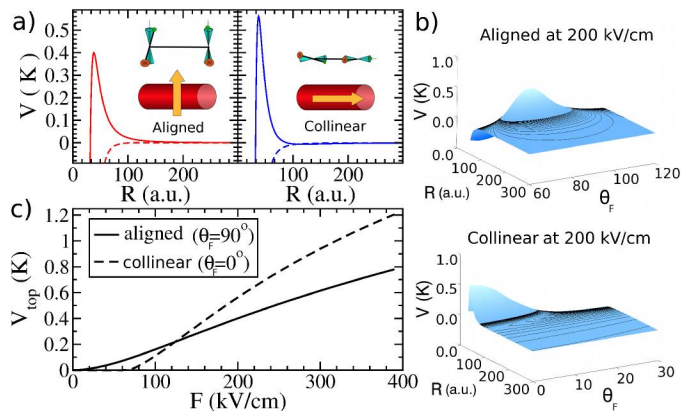

Figure 9: (a) KRb+KRb interaction (1-D) for weak (5 kV/cm: dashed lines) and strong electric field F (200 kV/cm: solid lines), for aligned and collinear orientations. (b) Interaction for both geometries vs. θ_F (angle of molecule and **F**). (c) Height of barrier vs. F.

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dimers [C10], where there are still anisotropic interactions, and extended it to the case of heteronuclear diatomic alkali molecules [C11]; in addition to the multipole expansion and van der Waals terms, we also give an analytic expression for molecules in an external (weak) DC electric field. Some of this work is summarized in a book chapter on polar molecules for quantum information processing [C12].

• Dressed and Rydberg states

We continued our initial work on interactions near the $69p + 71p$ [A3] and $69d + 70s$ [B4] asymptotes of ^{85}Rb, and its extension to study potential wells of doubly-excited atoms (macrodimers) due to ℓ-mixing [B5,B6], to explore metastable long-range *macrotrimers* made of three Rydberg atoms [C13]. We found shallow (~ 20 MHz deep) long-range wells for linear trimers. We also predicted the formation of bound states between two Rydberg atoms in an atomic condensate due to phonon exchange [C14].

We recently investigated Rydberg-dressed interactions (Fig. 10) in H_2+D [C15], using
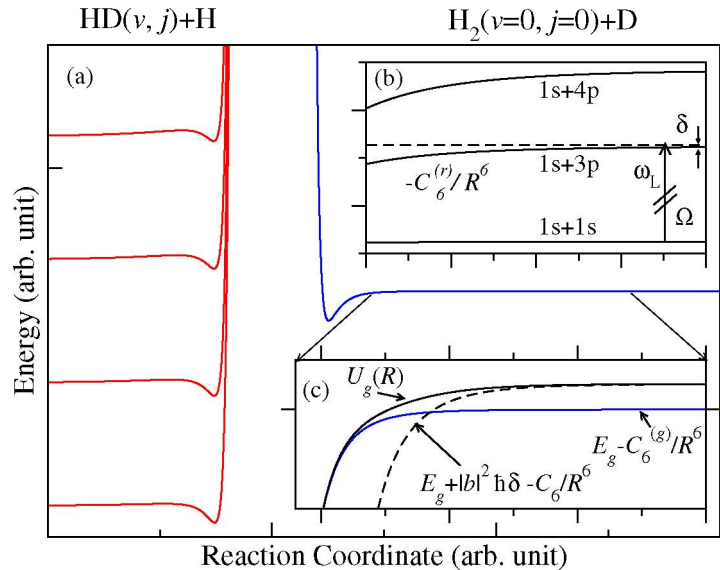

Figure 10: (a) Sketch of PES vs. reaction coordinates with exit (left) and entrance channels (right). (b) Rydberg dressing by blue-detuned laser ($\delta > 0$). (c) Long-range interaction: comparison of dressed $U_g(R)$ (solid black line) *bare* (blue solid line) curves.

$$\hat{H} = \begin{pmatrix} -C_6^{(g)}/R^6 & \hbar\Omega/2 \\ \hbar\Omega^*/2 & -\hbar\delta - C_6^{(r)}/R^6 \end{pmatrix}.$$

This dressed Hamiltonian, within the rotating wave approximation (RWA), describes the interaction of H_2 with D with its ground state g dressed with a Rydberg state r by a laser detuned by δ and Rabi frequency Ω. We showed in [C15] that Rydberg-dressed interactions could be used to tune $H_2+D\rightarrow HD+H$ chemical reactions.

• Formation of molecules

In previous papers sponsored by DOE [A1,A2,B1,B2], we explored the formation of diatomic molecules in their ground electronic state from one- and two-photon photoassociative processes. We also worked on using many coherent laser pulses [B3], and Feshbach resonances [B7] to increase the formation rate of ultracold diatomic molecules [B8-B10].

We recently explored how Feshbach resonances could enhance a pump-dump scheme to produce ground state LiRb molecules [C16], starting from the mixed $X\,^1\Sigma^+$ and $a\,^3\Sigma^+$ states at the Feshbach resonance being excited to $B\,^1\Pi$ by a pump pulse followed by a dump pulse into a target ro-vibrational level in the $X\,^1\Sigma^+$ ground state. To describe the transitions between $X\,^1\Sigma^+$ and $B\,^1\Pi$, we used the Hamiltonian (assuming RWA and dipole approximation)

$$\hat{\mathbf{H}} = \begin{pmatrix} \hat{\mathbf{T}} + V_{X^1\Sigma^+}(R) & \vec{\mu}(R) \cdot \vec{E}(t) \\ \vec{\mu}(R) \cdot \vec{E}(t) & \hat{\mathbf{T}} + V_{B^1\Pi}(R) - \hbar\omega_L \end{pmatrix},$$

where $\hat{\mathbf{T}}$ is the kinetic energy operator and $V_i(R)$ are the respective potential energy curves. We simulated the pump-dump PA process using a time-dependent wave packet approach (TDWP), assuming the laser pulse to be transform-limited $\vec{E}(t) = \vec{E}_0 f(t) \cos(\omega_L t)$ with a gaussian profile $f(t) = \exp[-\alpha(t - t_c)^2]$. We represented $\hat{\mathbf{H}}$ on a Fourier grid with a variable grid step, and solved the time-dependent Schrödinger equation ($i\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{\mathbf{H}}(t)\Psi(t)$), by expanding the evolution operator ($\exp[-i\hat{\mathbf{H}}t/\hbar]$) in terms of Chebyshev polynomials. We found that an increase of up to three orders of magnitude in the absolute number of molecules produced is attainable for deeply bound vibrational levels.

3.2   Publications sponsored by DOE: Current Period

C1. Jason N. Byrd, H. Harvey Michels, John A. Montgomery, Jr., and Robin Côté, *Long-range three-body atom-diatom potential for doublet Li$_3$*, Chem. Phys. Lett. **529**, 23 (2012).

C2. Jason N. Byrd, H. Harvey Michels, John A. Montgomery, Robin Côté, and William C. Stwalley, *Structure, energetics, and reactions of alkali tetramers*, J. Chem. Phys. **136**, 014306 (2012).

C3. Ion Simbotin, Subhas Ghosal, and Robin Côté, *Threshold resonance effects in reactive processes*, Phys. Rev. A **89**, 040701(R) (2014).

C4. Ionel Simbotin and Robin Côté, *Jost function description of near threshold resonances for coupled-channel scattering.* Chem. Phys. **462**, 79 (2015). (available on line July 2 2015).

C5. Ionel Simbotin and Robin Côté, *Effect of nuclear spin symmetry in cold and ultracold reactions: D + para/ortho-H$_2$.* New J. Phys. **17**, 065003 (2015).

C6. Sandipan Banerjee, John A. Montgomery, Jr., Jason N. Byrd, H. Harvey Michels, and Robin Côté, *Ab initio potential curves for the $X\ ^2\Sigma_u^+$, $A\ ^2\Pi_u$, and $B\ ^2\Sigma_g^+$ states of Ca_2^+*, Chem. Phys. Lett. **542**, 138-142 (2012).

C7. W. W. Smith, D.S. Goodman, I. Sivarajah, J.E. Wells, S. Banerjee, R. Côté, H.H. Michels, J.A. Montgomery Jr., and F.A. Narducci, *Experiments with an ion-neutral hybrid trap: cold charge-exchange collisions*, Appl. Phys. B **114**, 75 (2014).

C8. Jason N. Byrd, H. Harvey Michels, John A. Montgomery, Jr., and Robin Côté, *Associative detachment of rubidium hydroxide.* Phys. Rev. A **88**, 032710 (2013).

C9. Jason N. Byrd, John A. Montgomery, and Robin Côté, *Controllable Binding of Polar Molecules and Metastability of One-Dimensional Gases with Attractive Dipole Forces*, Phys. Rev. Lett. **109**, 083003 (2012).

C10. Jason N. Byrd, Robin Côté, and John A. Montgomery, *Long-range interactions between like homonuclear alkali metal diatoms*, J. Chem. Phys. **135**, 244307 (2011).

C11. Jason N. Byrd, John A. Montgomery, and Robin Côté, *Long-range forces between polar alkali-metal diatoms aligned by external electric fields*, Phys. Rev. A **86**, 032711 (2012).

C12. Robin Côté, *Ultracold molecules: their formation and application to quantum computing.* Advances in Chemical Physics **154**, Chap. 7, pp. 403-448, John Wiley and Sons (New York) (2014).

C13. Nolan Samboy and Robin Côté, *Rubidium Rydberg linear macrotrimers.* Phys. Rev. A **87**, 032512 (2013).

C14. Jia Wang, Marko Gacesa, and Robin Côté, *Rydberg Electrons in a Bose-Einstein Condensate.* Phys. Rev. Lett. **114**, 243003 (2015).

C15. Jia Wang, Jason N. Byrd, Ion Simbotin, and Robin Côté, *Tuning ultracold chemical reactions via Rydberg-dressed interactions.* Phys. Rev. Lett. **113**, 025302 (2014).

C16. M. Gacesa, S. Ghosal, J.N. Byrd, and R, Côté, *Feshbach-optimized photoassociation of ultra-cold $^6Li^{87}Rb$ molecules with short pulses*, Phys. Rev. A **88**, 063418 (2013).

3.3 Outreach/dissemination activities and Training

Research based on DOE support during Grant Period C was presented by the PI in a total of 10 invited talks at conferences/workshops (including ICPEAC 2013), 20 invited talks at universities, and 27 contributed talks/posters (with students/postdocs/colleagues) at conferences.

One High School student was involved in part of this research (Kaaviyan Faezi, Glastonbury High School). Four students were supported by DOE during the Grant Period C: Ionel Simbotin (Ph.D. 12), Sandipan Banerjee (Ph.D. 13), Jason Byrd (Ph.D. 13), and Di Shu. Two postdocs were supported during the current period: (Drs. Shubas Ghosal and Jia Wang) and one in previous periods (Dr. Philippe Pelligrini).

4 Collaborations with BES Supported Scientists

We have collaborated with several scientists supported by the DOE BES program. In three cases, this resulted in new collaborative projects: A. Dalgarno, D. DeMille, and N. Berrah. In one case the collaboration resulted in a publication [B13] on OH(J=3/2, M_J=3/2, f) molecules with ^{4}He atoms.