

Ultracold Collisions Involving Heteronuclear Alkali Metal Dimers

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We carry out the first quantum dynamics calculations on ultracold atom-diatom collisions in isotopic mixtures. The systems studied are spin-polarized ${}^7\text{Li} + {}^6\text{Li}{}^7\text{Li}$, ${}^7\text{Li} + {}^6\text{Li}_2$, ${}^6\text{Li} + {}^6\text{Li}{}^7\text{Li}$, and ${}^6\text{Li} + {}^7\text{Li}_2$. Reactive scattering can occur for the first two systems even when the molecules are in their ground rovibrational states, but is slower than vibrational relaxation in homonuclear systems. Implications for sympathetic cooling of heteronuclear molecules are discussed.

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The last few years have seen enormous advances in methods for producing ultracold molecules, both by direct cooling from room temperature and by dimer formation in cold atomic gases. Such molecules have potential applications in many fields, ranging from measurement of the dipole moment of the electron to quantum computation and cryptography. Of particular interest is the possibility of developing a novel ultracold chemistry based on precisely controlled collisions between state-selected molecules at precise relative velocities.

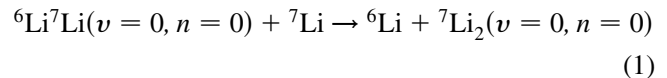
Ultracold heteronuclear dimers are of particular interest, both because they can be fermionic (whereas neutral homonuclear molecules cannot) and because there are new phases of matter predicted for quantum-degenerate dipolar gases. Formation of mixed alkali metal dimers by photoassociation has already been detected in cold atomic traps, [1–7] and magnetically tunable Feshbach resonances have very recently been observed experimentally in two such systems [8,9]. Efforts are under way to use these resonances for production of ultracold molecules. Cold bialkali dimers have also been formed on helium droplets [10].

The molecules (heteronuclear or homonuclear) produced so far from ultracold atomic gases have been formed in high vibrational states. These are prone to undergo inelastic collisions (quenching) with the remaining atoms or other molecules; the resulting recoil produces trap loss. In the case of homonuclear molecules, this difficulty was overcome by making use of fermionic isotopes (${}^6\text{Li}$ and ${}^{40}\text{K}$), and tuning the scattering length to very large positive values [11]. It was found that the inelastic collision rates were then significantly suppressed, and long-lived molecular Bose-Einstein condensates were produced at the end of 2003 [12–14]. Petrov *et al.* [15] have explained the suppression in terms of Pauli blocking.

Efforts are being made to produce alkali metal dimers in low-lying vibrational states, either directly or by transferring the population from high-lying states. However, we have shown computationally that Pauli blocking does *not* suppress inelastic collisions for low-lying vibrational states [16,17]. For such states the quenching rates dominate the

elastic rates below 1 mK even when fermionic isotopes are used. To trap homonuclear alkali metal dimers with small bond lengths, it will therefore be essential to produce them in their ground rovibrational state.

In the case of heteronuclear molecules the situation is even more complicated. Even if heteronuclear dimers are produced in their ground rovibrational states, the molecules may not be stable against collisions. For example, the spin-polarized reaction



is exothermic by 1.822 K because of the difference between the zero-point energies of the two dimers.

The focus of this Letter is the collision of lithium atoms with lithium dimers in cold atomic gases containing both the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes. We carry out the first full quantum dynamics calculations for spin-polarized collisions involving heteronuclear alkali metal dimers. They are also the first calculations on barrierless ultracold reactions in which the reactants and products are chemically distinct. We find that quenching via process (1), is significantly slower than the vibrational relaxation processes studied previously in homonuclear collisions [16]. In the present case the elastic cross section dominates the inelastic cross sections in a region between 10 μK and 10 mK.

Quantum scattering calculations require accurate potential energy surfaces. We have previously shown that the interaction potential for spin-polarized (quartet) $\text{Li} + \text{Li}_2$ is highly nonadditive [18], with a well depth 4 times that of the sum of three Li-Li triplet pair potentials. In the present work, we use a global quartet Li_3 potential obtained from all-electron coupled-cluster electronic structure calculations. This is the same potential as was used in our work on homonuclear $\text{Li} + \text{Li}_2$ collisions [16] and will be described in detail elsewhere [19].

The methods we use to carry out quantum dynamics calculations on systems of this type have been described in our previous work on $\text{Na} + \text{Na}_2$ [20,21], and elsewhere in

the context of thermal reactive scattering [22], so a brief summary will suffice here. The potential energy surface is barrierless, so that it is essential to take reactive (atom exchange) collisions into account. The positions of the nuclei are described in hyperspherical democratic coordinates. The configuration space is divided into inner and outer regions, and the boundary between them is placed at a distance such that couplings due to the residual atom-diatom interaction can be neglected outside the boundary. In the inner region (hyperradius $\rho \leq 45a_0$ in the present case), we obtain the wave function for nuclear motion by propagating a set of coupled equations in a diabatic-by-sector basis that is obtained by diagonalizing a fixed- ρ reference Hamiltonian in a basis set of pseudohyperspherical harmonics. In the outer region, we use the Arthurs-Dalgarno formalism [23], which is based on Jacobi coordinates, and compute by inwards integration regular and irregular solutions of a radial Schrödinger equation which includes the isotropic (R^{-6}) part of the interaction. Matching between wave functions in the inner and outer regions yields the scattering S matrix.

The present calculations deal with systems containing two nuclei that are identical and a third that is different. We consider spin-stretched states of all three atoms involved (states with $|M_F| = F = F_{\max}$), for which the nuclear spin wave function is symmetric with respect to any exchange of nuclei. However, the electronic wave function for the quartet state is antisymmetric with respect to exchange of nuclei because it depends parametrically on nuclear positions. Thus the wave function for nuclear motion must be antisymmetric with respect to exchange of the two identical bosonic nuclei (for fermionic alkali metal atoms) and symmetric with respect to exchange of the two identical fermionic nuclei (for bosonic alkali metal atoms).

Asymptotically, the hyperspherical functions correlate with atom-diatom functions; the diatom functions for Hund's case (b), which is appropriate for Li_2 ($^3\Sigma_u^+$), are labeled with a vibrational quantum number v and a quantum number n for the nuclear rotational motion; n couples with the diatomic electron spin $s = 1$ to give a resultant j , but for Li_2 the splittings between states of the same n but different j are very small and are neglected here. In the $^3\Sigma_u^+$ state, only even n is allowed for $^7\text{Li}_2$ and only odd n for $^6\text{Li}_2$. In the outer region, we include rovibrational states with $v = 0, 1, \dots, 7$ with all rotational levels up to $n_{\max} = 32, 29, 26, 23, 20, 17, 13,$ and 7 for $^7\text{Li}^6\text{Li}$, with all even rotational levels up to $n_{\max} = 32, 30, 28, 24, 22, 18, 14,$ and 10 for $^7\text{Li}_2$, and with all odd rotational levels up to $n_{\max} = 31, 27, 25, 21, 19, 15, 11,$ and 7 for $^6\text{Li}_2$. Because of the reduced symmetry, the present calculations are substantially more expensive than our previous ones on collisions involving three identical atoms, and we have restricted them to total angular momentum and parity $J^\Pi = 0^+$ and 1^- , excluding spin. The basis sets of pseudohyperspherical harmonics involved between 3660 and 6488 functions.

There are four collision systems of interest to $^6\text{Li}/^7\text{Li}$ mixtures:



We have calculated the low-energy elastic, inelastic, and reactive cross sections $\sigma(E)$ for all four of these collision systems, considering all energetically allowed processes for a variety of initial diatomic rovibrational states (v, n). The present Letter will focus on collisions with the diatomic molecule initially in its lowest allowed rovibrational state. Details of the results for other initial states may be found in Ref. [24].

At very low energies (up to about 1 mK), the cross sections are dominated by collisions with orbital angular momentum $l = 0$, for which there are no centrifugal barriers. The s -wave cross sections for $^7\text{Li} + ^6\text{Li}^7\text{Li}(v = 0, n = 0)$ are shown as a function of collision energy E in Fig. 1. There is an energetically allowed reactive pathway to form $^7\text{Li}_2(v = 0, n = 0) + ^6\text{Li}$; at collision energies above 0.477 K the $v = 0, n = 2$ state of $^7\text{Li}_2$ is also accessible.

Scattering calculations for $\text{Li} + \text{Li}_2$ are converged up to about 10^{-4} K using just a single partial wave. At higher energies, other partial waves start to contribute significantly. It may be seen in Fig. 1 that the reactive cross section for $^7\text{Li} + ^6\text{Li}^7\text{Li}(v = 0, n = 0)$ at 10^{-4} K is 6.7×10^{-14} cm², corresponding to a limiting low-temperature rate coefficient $k_{\text{loss}} = 4.1 \times 10^{-12}$ cm³ s⁻¹. This is about 2 orders of magnitude smaller than obtained previously for $^6\text{Li} + ^6\text{Li}_2(v > 0)$ and $^7\text{Li} + ^7\text{Li}_2(v > 0)$ [16]; the differ-

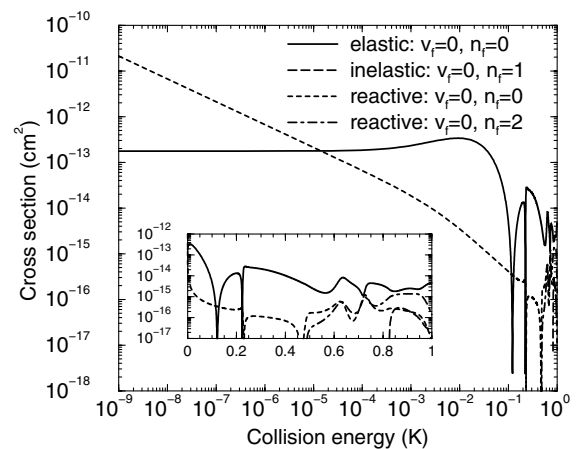


FIG. 1. Elastic and reactive s -wave cross sections for $^7\text{Li} + ^6\text{Li}^7\text{Li}(v = 0, n = 0)$. The inset shows the higher-energy cross sections on a log-linear scale, with axes in the same units as the main plot.

ence is present only for the initial state $v = 0, n = 0$, and can be attributed to the existence of only a single product rovibrational channel in that case. As a result, elastic scattering dominates reactive scattering for ${}^7\text{Li} + {}^6\text{Li}^7\text{Li}(v = 0, n = 0)$ at collision energies between 10 μK and 10 mK. (The upper limit is uncertain because the partial wave sum is not converged at higher energies.)

The existence of a low-energy closed product channel increases the density of low-energy Feshbach resonances. These are most conveniently detected by plotting the S matrix eigenphase sum $\varsigma(E)$ [25] as a function of energy: at a resonance, $\varsigma(E)$ increases sharply by π , superimposed on a falling background. The eigenphase sum for ${}^7\text{Li} + {}^6\text{Li}^7\text{Li}$ is shown as a function of energy above the $v = 0, n = 0$ threshold in Fig. 2. There are clear isolated resonances at 225 and 470 mK and a pair of overlapping resonances at about 630 and 725 mK. The cusp at 825 mK corresponds to the opening of the $(v = 0, n = 1)$ reactant channel. Small changes in the potential energy surface might result in significant changes in the positions of individual resonances, but the *density* of resonances obtained here should be realistic. However, it should be remembered that the present calculations neglect nuclear spin and magnetic fields, which produce additional resonance structures and ways to tune them.

For ${}^6\text{Li} + {}^6\text{Li}^7\text{Li}(v = 0, n = 0)$, the reactive channel to form ${}^6\text{Li}_2$ is closed at energies below 2.643 K and only elastic scattering is possible. The low-energy limit of the cross section is $4.7 \times 10^{-12} \text{ cm}^2$.

For ${}^6\text{Li}_2$, the lowest allowed rotational level is $n = 1$. For ${}^7\text{Li} + {}^6\text{Li}_2(v = 0, n = 1)$, the lowest partial wave to include an $l = 0$ incoming channel is therefore $J^\Pi = 1^-$. The corresponding cross sections are shown as a function of collision energy E in Fig. 3. The species can either collide elastically or react exothermically to form ${}^6\text{Li}^7\text{Li} + {}^6\text{Li}$ with the diatom in its $(0,0)$, $(0,1)$, and $(0,2)$ states, with kinetic energy releases of 2.643, 1.1818, and 0.157 K, respectively. In this case the reactive cross section at 10^{-4} K is $7.1 \times 10^{-13} \text{ cm}^2$, which corresponds to a

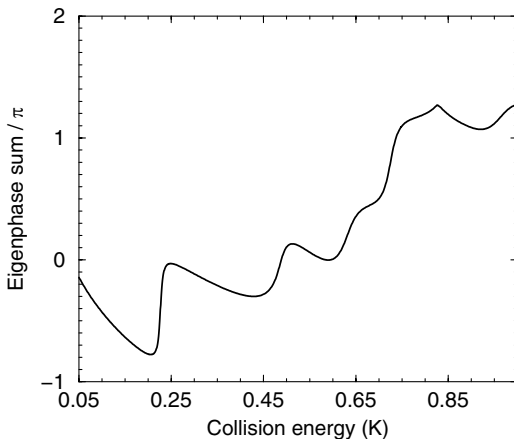


FIG. 2. Eigenphase sum for ${}^7\text{Li} + {}^6\text{Li}^7\text{Li}(J^\Pi = 0^+)$.

limiting low-temperature rate coefficient $k_{\text{loss}} = 4.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. This is considerably larger than for ${}^7\text{Li} + {}^6\text{Li}^7\text{Li}(v = 0, n = 0)$, though the *partial* cross section to form the $(v = 0, n = 0)$ product is comparable; the larger value for the *total* reactive cross section reflects the increased number of open product channels for ${}^7\text{Li} + {}^6\text{Li}_2(v = 0, n = 1)$.

For ${}^6\text{Li} + {}^7\text{Li}_2(v = 0, n = 0)$ the reactive channel to form ${}^6\text{Li}^7\text{Li}$ is closed at energies below 1.822 K and only elastic scattering is possible. The low-energy limit of the cross section is $1.3 \times 10^{-12} \text{ cm}^2$.

The results obtained here have important implications for experiments aimed at producing a quantum gas of ${}^6\text{Li}^7\text{Li}$ in its ground rovibronic state in an ultracold mixture of ${}^6\text{Li}$ and ${}^7\text{Li}$ atoms. In order to stabilize the molecular cloud against two-body trap losses induced by the reactive process (1), the remaining atomic ${}^7\text{Li}$ must be removed quickly after ground-state molecule production, so that just the two-species fermionic mixture of ${}^6\text{Li}^7\text{Li}(v = 0, n = 0)$ molecules and ${}^6\text{Li}$ atoms is left in the trap. One could separate the ${}^6\text{Li}$ atomic cloud from the molecular cloud as well, but it might be advantageous to keep them both in the trap. It has been observed that in a one-component dilute Fermi gas the s -wave collisions are strongly suppressed because of Pauli blocking [26]. This will make evaporative cooling of the molecular cloud very inefficient. However, to achieve further cooling of the ${}^6\text{Li}^7\text{Li}(v_i = 0, n_i = 0)$ molecules, a sympathetic cooling scheme might be developed. Sympathetic cooling of fermionic molecules can be approached from two directions: interstate or inter-species sympathetic cooling.

Interstate sympathetic cooling is based on s -wave collisions between particles of the same species but in two different states. It was previously used, for example, to produce two overlapping Bose-Einstein rubidium condensates [27] and to create a Fermi sea from potassium atoms [28]. Unfortunately, for ${}^6\text{Li}^7\text{Li}$ there are various inelastic processes resulting from reactive molecule + molecule

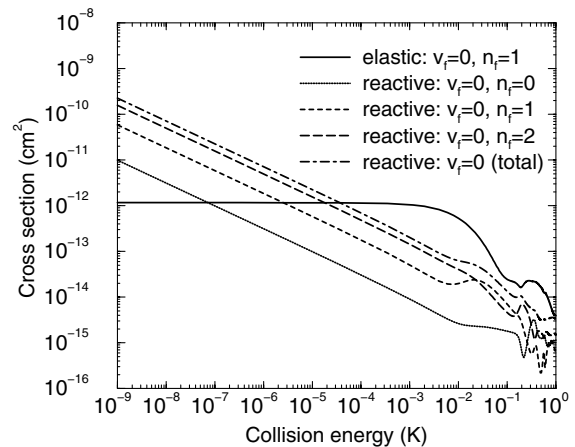


FIG. 3. Elastic and reactive cross sections for ${}^7\text{Li} + {}^6\text{Li}_2(v = 0, n = 1)$ with $J^\Pi = 1^-$.

s -wave collisions that are likely to produce significant trap losses. It will therefore be better to keep the molecules in the same state, where Pauli blocking suppresses such processes.

Interspecies sympathetic cooling makes use of s -wave collisions between two different species. It has been used to produce a Bose-Einstein condensate of atomic potassium [29] and to create a two-species mixture of quantum-degenerate Bose and Fermi gases [30]. In the present case we can distinguish two interspecies sympathetic cooling schemes.

The first scheme uses the fact that ultracold collisions between spin-stretched ${}^6\text{Li}{}^7\text{Li}(\nu = 0, n = 0)$ and ${}^6\text{Li}$ can result only in elastic scattering, because the corresponding inelastic and reactive processes are energetically forbidden. Thus no undesirable quenching-induced trap loss occurs. The elastic collisions will then lead to sympathetic cooling between the atomic and molecular clouds. This could be done in the trap where the molecules were produced, or alternatively the ${}^6\text{Li}{}^7\text{Li}$ molecules could be transported into a reservoir of colder ${}^6\text{Li}$ atoms. This scheme is similar to interstate sympathetic cooling for fermions in the sense that neither of the components can be cooled evaporatively and the cooling is done only by interspecies collisions.

If the efficiency of the first scheme is not high enough to achieve quantum degeneracy in the molecular cloud, then an alternative will need to be adopted. One possibility is to transport the molecular cloud into a reservoir of bosonic atoms such as ${}^{87}\text{Rb}$. Spin-polarized ultracold collisions between ${}^6\text{Li}{}^7\text{Li}(\nu = 0, n = 0)$ and an alkali metal atom heavier than Li can lead only to elastic scattering, because the reactive quenching channels are not energetically accessible. The bosonic component can then be cooled evaporatively. Note, however, that this will work only if both species are in spin-stretched states, as collisions involving other states could produce reaction to form singlet states of molecules such as LiRb.

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