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Ultracold Li + Li₂ Collisions: Bosonic and Fermionic Cases

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We have carried out quantum dynamical calculations of vibrational quenching in Li + Li₂ collisions for both bosonic ⁷Li and fermionic ⁶Li. These are the first ever such calculations involving fermionic atoms. We find that for the low initial vibrational states considered here ($v \leq 3$), the quenching rates are *not* suppressed for fermionic atoms. This contrasts with the situation found experimentally for molecules formed via Feshbach resonances in very high vibrational states.

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There is at present great interest in the properties of cold and ultracold molecules. At the end of 2003, three groups [1–3] created long-lived molecular Bose-Einstein condensates from ultracold atomic gases by making use of magnetically tunable Feshbach resonances. The molecules are formed in highly excited vibrational states, and any vibrational relaxation will result in trap loss. A crucial breakthrough was the use of fermionic isotopes of the atomic gases (⁶Li, ⁴⁰K) tuned to large positive scattering lengths; it was found that in this case the atom-molecule and molecule-molecule inelastic collisions are strongly suppressed [4–7], and the molecular cloud consisting of weakly bound dimers of fermions exhibits a remarkable stability against collisional decay. By contrast, for weakly bound dimers of bosonic atoms the vibrational relaxation is fast, so that the corresponding molecular cloud decays quickly and quantum degeneracy can be achieved only transiently [8–12]. Petrov *et al.* [13] have explained the important difference between molecular gases of weakly bound dimers formed from bosonic and fermionic atoms in terms of different quantum statistics for the atoms.

In this Letter, we carry out the first full quantum dynamics calculations for spin-polarized collisions of ultracold homonuclear molecules for Li + Li₂ in both the bosonic (⁷Li) and fermionic (⁶Li) cases. We find that for low-lying vibrational states there is no systematic suppression of the vibrational relaxation (quenching) rates for fermions, even when the scattering length is large and positive. The analysis of Petrov *et al.* [13] applies only when the scattering length is large and positive *and* the molecules are in their highest-lying vibrational state.

Quantum scattering calculations require accurate potential energy surfaces. We have previously shown that the interaction potential for spin-polarized (quartet) Li + Li₂ is highly nonadditive [14], with a well depth 4 times that of the sum of Li-Li pair potentials. In the present work, we use a global Li₃ potential obtained from all-electron coupled-cluster electronic structure calculations, which will be described in detail elsewhere [15]. In parallel

work, Colavecchia *et al.* [16] have obtained another potential surface based on pseudopotential calculations. However, we chose to use our own surface in the present work because it takes better account of some features of the potential. In particular, as pointed out in Ref. [14], there is a seam of conical intersections at collinear geometries, between the ⁴Σ surface that is the ground state at long range and a ⁴Π surface that becomes the ground state inside $r_1 = r_2 = 3.1$ Å. The resulting cusp drops to energies very close to the atom-diatom threshold, as shown in Fig. 1, and so may play a significant role in the dynamics.

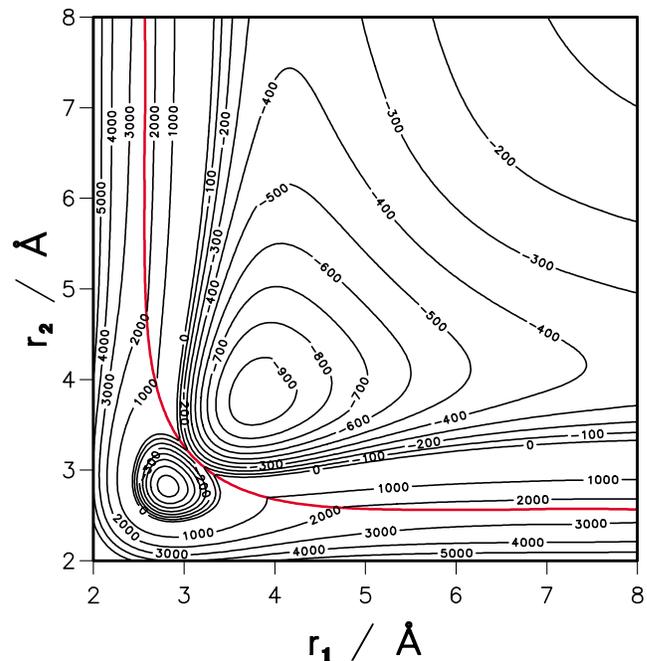


FIG. 1 (color online). A cut through Li₃ quartet surface at collinear geometries, showing the seam between ⁴Σ and ⁴Π states. Contours are labeled in cm⁻¹. The two minima are at depths of 760 and 950 cm⁻¹.

Our potential takes better account of this seam than that of ref. [16].

The methods we use to carry out quantum dynamics calculations on systems of this type have been described in our previous work on Na + Na₂ [17,18] and elsewhere in the context of thermal reactive scattering [19], so a brief summary suffices 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 [20], 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 difference between the ⁶Li and ⁷Li cases is implemented by selecting the pseudohyperspherical harmonic basis functions included in the basis set. For both bosons and fermions, we consider spin-stretched states of all three atoms involved (states with $|M_F| = F = F_{\max}$). For such states 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. Thus, to satisfy the Pauli principle, the wave function for nuclear motion must be antisymmetric with respect to exchange of bosonic nuclei (for fermionic alkali metal atoms) and symmetric with respect to exchange of 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 Li₂(³Σ_u⁺), are labeled with a vibrational quantum number v and a mechanical rotational quantum number n ; n couples with the diatomic electron spin $s = 1$ to give a resultant j , but for Li₂ the splittings between states of the same n but different j are very small and are neglected here. In the ³Σ_u⁺ state, only even n is allowed for ⁷Li₂ and only odd n for ⁶Li₂. In the outer region, we include rovibrational states with $v = 0, 1, \dots, 7$ with all even rotational levels up to $n_{\max} = 32, 30, 28, 24, 22, 18, 14, 10$ for bosonic ⁷Li₂ and rovibrational states with $v = 0, 1, \dots, 7$ with all odd rotational levels up to $n_{\max} = 31, 27, 25, 23, 19, 17, 13, 7$ for fermionic ⁶Li₂. In the inner region, the number of coupled

equations for bosonic atoms varies from 97 for total angular momentum $J = 0$ to 827 for $J = 10$, and for fermionic atoms it varies from 85 for $J = 0^+$ to 782 for $J = 11^-$.

We have calculated the low-energy elastic and total quenching cross sections $\sigma(E)$ for ⁷Li₂ colliding with ⁷Li and for ⁶Li₂ colliding with ⁶Li, for bosons and fermions in all allowed initial states (v, n) with $v \leq 3$ and $n \leq 11$. The cross sections for $v = 1$ (with $n = 0$ for ⁷Li₂ and $n = 1$ for ⁶Li₂) are shown as a function of collision energy E in Figs. 2 and 3, together with the contributions from individual partial waves J . The partial wave sums are converged up to 500 mK for $J_{\max} = 10$. For $v = 1$, both the elastic and inelastic cross sections are slightly smaller for ⁶Li than for ⁷Li at energies below 1 mK. However, the difference is only about a factor of 2, and it is *not* due to the difference between boson and fermion symmetries: for other values of v and n the ratio is often reversed.

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. A consequence of the symmetry constraints is that total angular momentum $J = 0$ has an $l = 0$ channel for ⁷Li + ⁷Li₂ but not for ⁶Li + ⁶Li₂; in the latter case the lowest partial wave containing $l = 0$ is $J = 1^-$, where the superscript indicates odd parity. For this reason, low-energy calculations on ⁶Li are significantly more expensive than those on ⁷Li.

For nearly all initial v and n , and for both bosons and fermions, the ratio of inelastic to elastic cross sections is greater than 30 at $E = 1 \mu\text{K}$ and remains greater than 1 throughout the Wigner regime (i.e., up to about 1 mK). The only exceptions to this are for rotational quenching of the $(v, n) = (0, 2)$ state for bosons (ratio 4.3 at 1 μK) and the $(0, 3)$ state for fermions (ratio 7.5), for which there is only one inelastic channel with $l = 0$.

Scattering calculations for Li + Li₂ are converged up to about 10^{-4} K using just a single partial wave ($J = 0$ for ⁷Li and $J = 1^-$ for ⁶Li). At higher energies, other partial waves start to contribute significantly. For ⁷Li the contributions decrease monotonically with J at low energies because of centrifugal barriers corresponding to $l = J$ for $n = 0$. For ⁶Li, the situation is slightly different: each partial wave is made up of a "parity favored" block [with parity $(-1)^J$] and a "parity unfavored" block; the former includes an $n = 1$ channel with $l = J - 1$, while for the latter the lowest l is $l = J$.

At collision energies below the centrifugal barrier, the partial cross sections follow Wigner laws, $\sigma_{\text{inel}}^l \sim E^{l-1/2}$. Since $k_{\text{inel}}(E) = v_{\text{coll}} \sigma_{\text{inel}}(E)$, where $v_{\text{coll}} = (2E/\mu)^{1/2}$ is the collision velocity and μ is the atom-diatom reduced mass, the inelastic rate coefficient is independent of E at limitingly low energies. For initial $v = 1$, the results in Figs. 2 and 3 give calculated limiting values $k_{\text{inel}} = 5.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for bosons and $2.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for fermions.

At energies above the barrier height, the inelastic probabilities saturate at values close to 1 and the energy dependence in each partial wave is then governed by the prefactor E^{-1} that multiplies the S -matrix term in the expression for the cross section. At energies high enough that several partial waves (typically >3) contribute significantly to the overall cross sections, the energy dependence is described approximately by classical Langevin capture theory [21],

$$k_{\text{inel}}(E) = 3\pi(2E/\mu)^{1/2} \left(\frac{C_6}{4E} \right)^{1/3}, \quad (1)$$

where $C_6 = 3086E_h a_0^6$ is the isotropic atom-diatom dispersion coefficient. The Langevin result is compared with the full quantum results for the quenching rates for $v = 1$ and 2 in Fig. 4; it may be seen that the Langevin and full quantum results agree semiquantitatively at collision energies above about 10 mK for both bosons and fermions.

The atom-atom part of the potential used in our calculations gives triplet scattering lengths that are approxi-

mately correct for both ${}^7\text{Li}$ ($-26.35a_0$) and ${}^6\text{Li}$ ($-1531a_0$). However, at the magnetic field used in the molecule production experiments [1], the spin states involved had $a \approx +3500a_0$, and it is important to establish whether fermionic suppression of quenching rates occurs for such large positive atom-atom scattering lengths. We have therefore repeated the calculations for energies $E = 1 \mu\text{K}$ and 1 nK with the short-range part of the two-body potential adjusted to reproduce $a \approx 3500a_0$. This was done by adding a small term $A(r - r_e)^2$ to each atom-atom potential for $r < r_e = 7.8852a_0$, while keeping the three-body potential (and the long-range part of the two-body potential) fixed. Slightly different adjustments were needed for ${}^7\text{Li}$ ($A = -27.6 \text{ cm}^{-1} a_0^{-2}$) and ${}^7\text{Li}$ ($A = -1.782 \text{ cm}^{-1} a_0^{-2}$). Under these circumstances the calculated quenching rates for initial $v = 1$ at limitingly low energy are $7.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for ${}^7\text{Li}$ and $2.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for ${}^6\text{Li}$. This confirms that there is no fermionic suppression for the low-lying states that we consider.

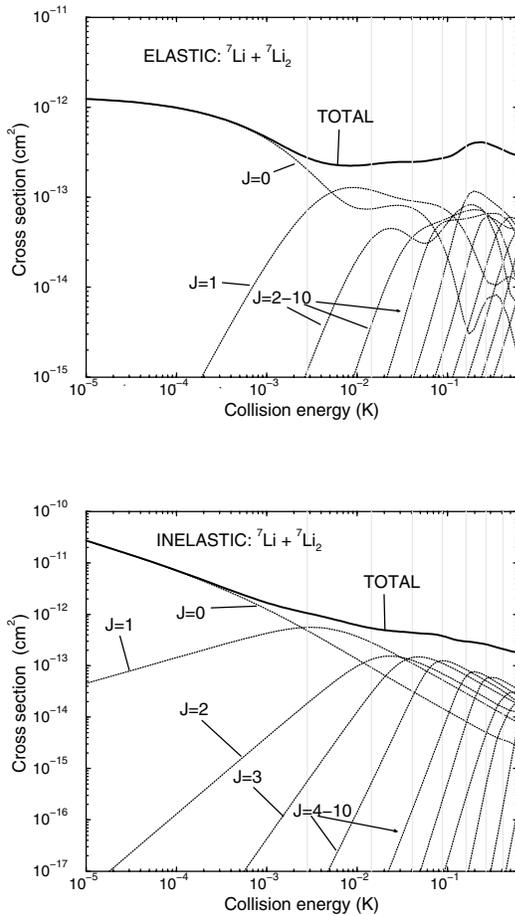


FIG. 2. Elastic cross sections (upper panel) and inelastic cross sections (lower panel) for ${}^7\text{Li} + {}^7\text{Li}_2$ ($v_i = 1, n_i = 0$), with contributions from individual partial waves. The vertical lines indicate centrifugal barrier heights for $l \geq 1$.

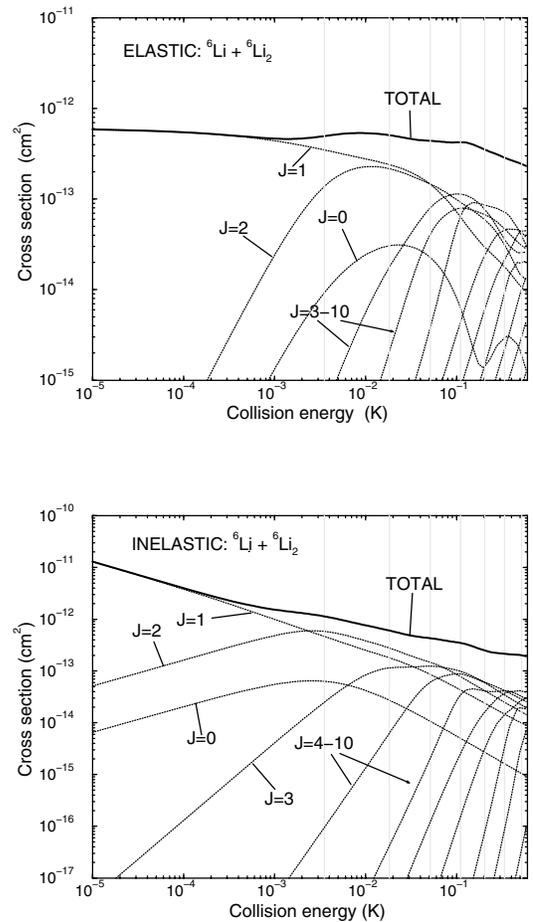


FIG. 3. Elastic cross sections (upper panel) and inelastic cross sections (lower panel) for ${}^6\text{Li} + {}^6\text{Li}_2$ ($v_i = 1, n_i = 1$), with contributions from individual partial waves. The vertical lines indicate centrifugal barrier heights for $l \geq 1$.

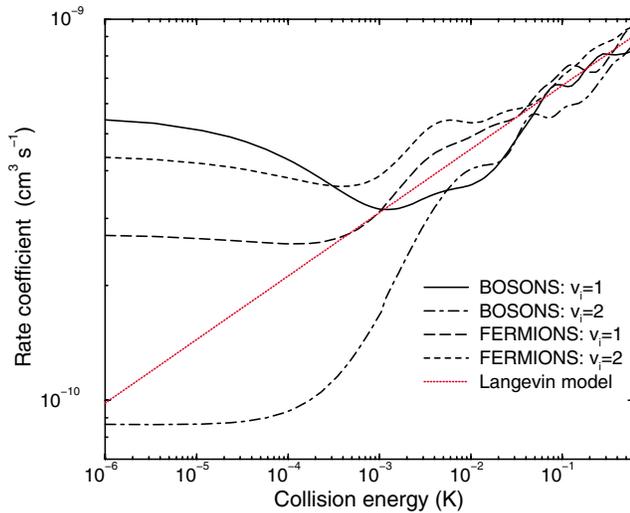


FIG. 4 (color online). Total inelastic rate coefficients for collisions of Li with Li_2 ($\nu = 1$ and 2, with $n = 0$ for bosons and $n = 1$ for fermions).

The Langevin result, Eq. (1), may be used to predict inelastic rates for other atom-diatom alkali systems in spin-polarized states. Outside the Wigner regime, the inelastic rate coefficients for different systems will be proportional to $C_6^{1/3}/\mu^{1/2}$. The resulting inelastic rate coefficients for ^{23}Na , ^{40}K , ^{87}Rb , and ^{133}Cs are lower than that for lithium by factors of 1.81, 1.75, 2.43, and 2.65, respectively, using C_6 coefficients equal to twice the atomic dispersion coefficients from Ref. [22]. The lower bound of applicability of the model may be estimated from the centrifugal barrier heights for $l = 3$, which are 6.86, 1.89, 0.537, and 0.235 mK, for Na, K, Rb, Cs, respectively.

In conclusion, we have carried out full quantum dynamics calculations of vibrational relaxation (quenching) of $^7\text{Li}_2$ by ^7Li and of $^6\text{Li}_2$ by ^6Li , taking full account of the boson and fermion symmetries. We find that for low initial vibrational states of the molecules ($\nu \leq 3$), there is *no* systematic suppression of the quenching rates for molecules formed from fermionic atoms, even when the atom-atom scattering length is large and positive. This contrasts with the situation for molecules formed in the highest vibrationally excited state [1–3].

Collisions of molecules involving *mixed* isotopes offer fascinating new possibilities and in some cases allow identifiable chemical reactions even between ground-state molecules. For example, the reaction $^7\text{Li} + ^6\text{Li}_2$ ($\nu = 0$) \rightarrow $^6\text{Li} + ^6\text{Li}^7\text{Li}$ ($\nu = 0$) is exothermic by 2.643 K be-

cause of the difference in zero-point energy of the two diatomic molecules. Calculations on collisions such as this will be described in future work.

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