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Ultracold collisions between Li atoms and Li_2 diatoms in high vibrational states

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We have performed a quantum-dynamical study of vibrational deexcitation and elastic scattering at ultralow collision energies for the bosonic system $^7Li+^7Li_2$ and for the fermionic system $^6Li+^6Li_2$ with diatomic molecules in *high* vibrational states. Inelastic rates show a strong and irregular dependence on the vibrational state of the diatomic molecule. For the highest vibrational state which lies near the dissociation limit, vibrational deexcitation processes are not suppressed, but rather depleted, for both bosonic and fermionic systems.

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Recently, molecular Bose-Einstein condensates (BECs) of $^{40}K_2$ [1] and $^6Li_2$ [2–4] have been produced. In these experiments, magnetically tunable Feshbach resonances [5] have been used to convert an ultracold degenerate Fermi gas of ^{6}Li atoms or ^{40}K atoms into an ultracold condensed gas of bosonic molecules. The atom-atom scattering length is tuned to very large and positive values, and inelastic processes are suppressed by the Pauli blocking mechanism as suggested by Petrov *et al.* [6]. In the experiments, the molecules are produced in high vibrational states which lie very close to the dissociation limit.

Up to now, only a few theoretical quantum-mechanical studies of molecular collisions with atom exchange in the ultralow-energy range have been reported for systems of experimental interest (for a review see [7]). We first studied $Na+Na_2$ $(v,j=0)$ elastic and inelastic scattering, with all bosonic Na atoms in the Na_3 system assumed to lie in spin-stretched states and the diatom lying in the vibrational states $v=1$, 2, 3 [8,9]. The sensitivity of the dynamics to the three-body part of the interaction has also been studied [9]. State-to-state cross sections were found to be very sensitive to three-body effects; however, total cross sections were less sensitive, especially for excited vibrational states $(v=2,3)$. We also performed quantum-dynamical calculations of spin-polarized $K+K_2$ collisions with fermionic ^{40}K atoms [10] and $Li+Li_2$ with fermionic or bosonic Li atoms [11,12]. The main conclusion of these studies was that no suppression of inelastic processes happens for bosonic or fermionic systems. However, the molecules were in low vibrational states $(v\leq 3)$ whereas they are in high vibrational states in the experiments on ultracold condensed molecules as mentioned above.

In this paper, we present a quantum-dynamical study of ultracold collisions between $Li(^2S)$ atoms and $Li_2(^3\Sigma_u^+)$ molecules for all initial vibrational states v. We consider three identical spin-polarized atoms with $F=I+S$ and $M_F=F$ ($F=3/2$ for the fermionic atom ^{6}Li and $F=2$ for the bosonic atom ^{7}Li).

We performed three-dimensional time-independent quantum dynamical calculations for $^7Li+^7Li_2$ and $^6Li+^6Li_2$ collisions including atom exchange. We used the potential energy surface of Colavecchia *et al.* [13] for the lowest quartet state $1\,^4A_2'$ of Li_3. At ultralow energies, only partial waves with orbital angular momentum $l=0$ contribute. Their total angular momenta and parity are $J^\Pi=0^+$ for the system with bosonic lithium and $J^\Pi=1^-$ for the system with fermionic lithium. The configuration space is divided into an inner and an outer region depending on the hyperradius ρ. In the inner region, we use a quantum formalism based on body-frame-symmetric hyperspherical coordinates [14,15] which has succesfully described atom-diatom insertion reactions such as $O(^1D)+H_2\rightarrow OH+H$ [16] and $N(^2D)+H_2\rightarrow NH+H$ [17] at thermal energies. For each hyperradius ρ, we determine a set of eigenstates and eigenvalues of a fixed hyperradius reference Hamiltonian $H_0=T+V$. This reference Hamiltonian incorporates the kinetic energy T arising from deformation and rotation around the axis of least inertia and the potential energy V. At small hyperradius, the eigenstates span a large fraction of configuration space and allow for atom exchange. We use a pseudo-hyperspherical-harmonics basis to diagonalize the reference Hamiltonian H_0. The pseudo-hyperspherical-harmonics basis is truncated at Λ_{max}, the maximum value of the grand angular momentum. Λ_{max} depends on ρ and varies from 198 (867 harmonics) at small ρ to 558 (6625 harmonics) at large ρ. Then, the scattering wave function is expanded on the set of hyperspherical adiabatic states. This yields a set of close-coupling equations, which are solved using the Johnson-Manolopoulos log-derivative propagator [18,19].

Figure 1 shows a typical set of $^7Li_3$ $(J^\Pi=0^+)$ adiabatic energies for the lowest 268 hyperspherical states as a function of the hyperradius ρ. At large hyperradius, there are two kinds of hyperspherical adiabatic states. The ones with negative energies describe configurations where an atom is far away from two others, forming a diatomic molecule lying in a specific rovibrational bound state, and will be called simple-continuum states (SCSs). The ones with positive energies decreasing as $1/\rho^2$ to zero (the origin in energy for three separated atoms with zero velocity) describe configurations where all three atoms can be far away from each other and will be called double-continuum states (DCSs). These states have to be included in calculations with mol-

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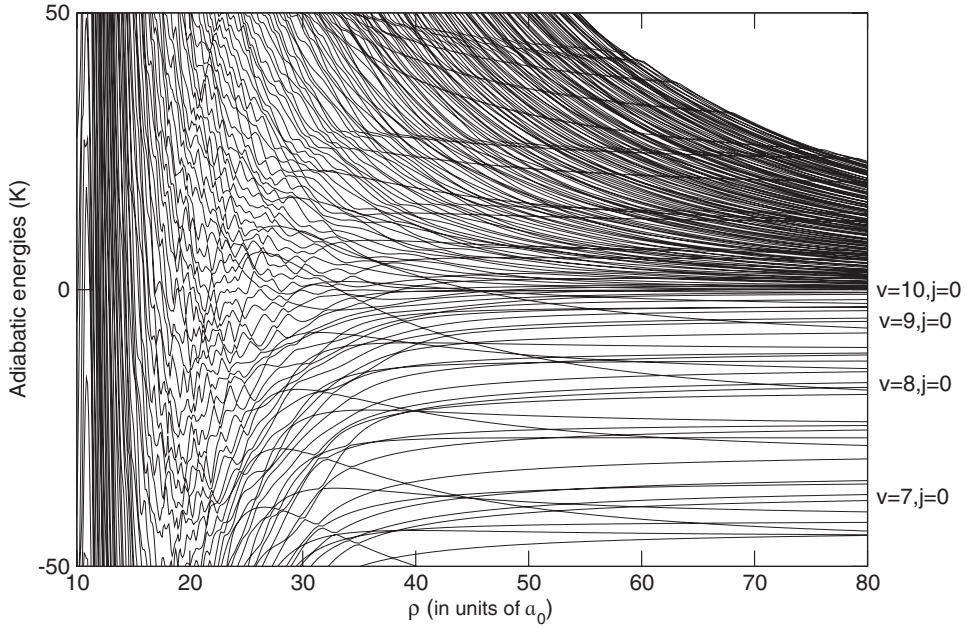


FIG. 1. Hyperspherical adiabatic energies (in kelvin) as a function of the hyperradius ρ for Li_3 ($J^{\Pi}=0^+$). The zero of energy is taken as the dissociation limit to three atoms. The curves which are asymptotically above the dissociation limit represent the double-continuum states (150 here) and the other ones which are asymptotically below represent the simple continuum states (see text).

ecules in high vibrational states. They are also important in processes such as collision-induced dissociation and three-body recombination [20,21]. For $^7Li_3$, the total number of SCSs is 118 for $J^{\Pi}=0^+$. Figure 1 shows also the energies of $^7Li_2$ $(v,j=0)$ rovibrational states with $v=[7-10]$. The total number of DCSs is actually infinite but we have to truncate the expansion of the wave function to a finite number of them. We will see below that we have to include a large number of these states to describe accurately the dynamics, especially for diatoms which are initially in high vibrational states.

In the outer region, for hyperradii larger than $\rho_{max}=80a_0$, we use the standard Arthurs-Dalgarno formalism [22] based on Jacobi coordinates for the SCSs. This value of ρ_{max} is large enough to obtain all the vibrational states of both diatomic molecule of $^7Li_2$ and $^6Li_2$ and small enough to spare computational time using hyperspherical coordinates. We assume that no coupling occurs between the closed DCSs and the SCSs for hyperradii larger than ρ_{max}. The boundary is chosen in such a way that residual couplings between rovibrational states of the diatom can be neglected and that the expansion of the wave function on double-continuum states is negligible. Then, the atom-diatom interaction can be described by an isotropic potential $U(R)$ and no inelastic scattering occurs in the outer region. We compute by inward integration from a very large distance (10^4a_0) regular and irregular solutions of a radial Schrödinger equation which includes the isotropic R^{-6} part of the interaction [23]. The matching of the inner and outer wave functions is performed on the boundary which is an hypersphere of radius ρ_{max}. This yields the scattering S matrix from which we compute cross sections and rate coefficients.

Rate coefficients for elastic and inelastic scattering at a collision energy of 10^{-9} K are shown in Fig. 2 for the $^7Li+^7Li_2$ $(v,j=0)$ bosonic collision and in Fig. 3 for the $^6Li+^6Li_2$ $(v,j=1)$ fermionic collision as a function of the vibrational quantum number v. The number of SCSs is 118 for $^7Li_3$ for $J^{\Pi}=0^+$ and 194 for $^6Li_3$ for $J^{\Pi}=1^-$ (97 for each value 0 or 1 of the projection of J on the axis of least inertia). Only deexcitation can occur for inelastic processes at ultralow energy. Several calculations which include all SCSs and an increasing number N of DCSs have been performed.

For the bosonic system, we see that inelastic rates are converged up to $v=2$ only and elastic rates up to $v=3$ only if one neglects DCSs. Including DCSs changes dramatically the rate coefficients for higher vibrational states. The energies of the DCSs go to zero as the hyperradius increases (see Fig. 1), and their density is very high close to the dissociation limit of the three atoms. Therefore, it is necessary to include a large number of them to obtain convergence for diatomic molecules in high vibrational states. Figure 2 shows that DCSs are very important to describe the dynamics accurately, even for low initial vibrational states such as $v=4$, and that it is necessary to include up to 1150 DCSs to obtain converged rate coefficients.

We also see in Fig. 2 that the inelastic rate decreases sharply as v increases from 9 to 10. This behavior can be understood qualitatively as follows. When the diatomic molecule is in the highest vibrational level $v=10$, the two atoms spend a large part of their time near the outer turning point of the diatomic potential, far away from each other and with low velocities. When a third atom approaches very slowly, it will collide with one of the two atoms of the diatom, very far away from the other one. Because of their small velocities, the change in their kinetic energy will be very small and vibrational deexcitation inefficient. This effect has already been suggested by Stwalley [24] and seen in the $H+H_2$ reaction [25,26]. However, this depletion is not important enough to make elastic processes faster than inelastic ones.

For the fermionic system, two projections of J are needed and roughly twice as many states have to be included to converge rate coefficients. Because of computer limitations, we can include 800 DCSs and converge only half of the rates. However, we see in Fig. 3 that the rate for the highest vibrational state $v=9$ is converged. Convergence is faster for

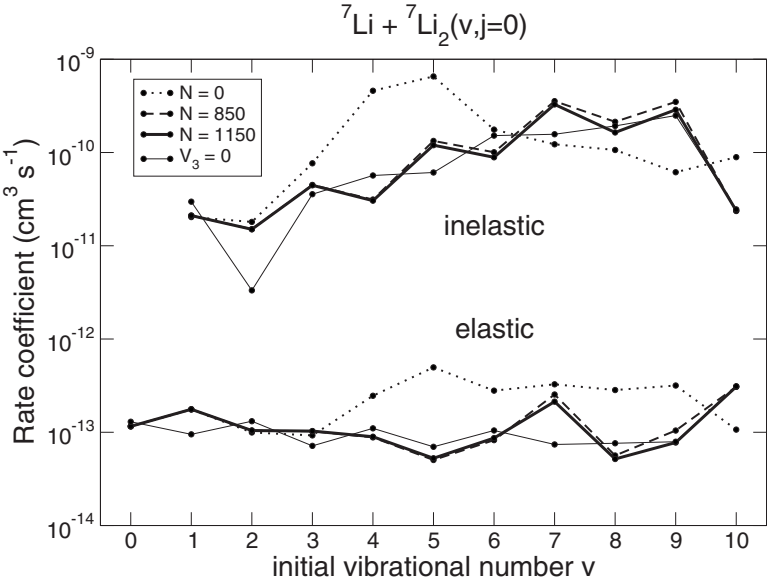


FIG. 2. Elastic and inelastic rate coefficients for ^{7}Li+^{7}Li$_2$ $(v,j=0)$ (bosonic isotopes) for $N=0$ (dotted curve), $N=850$ (dashed curve), $N=1150$ (bold solid curve), and $N=1150$ without three-body potential (solid curve), where N is the number of double-continuum states. The collision energy is 10^{-9} K.

this state than for the $v=5-8$ states because for $v=9$ the three atoms spend a large part of their time far away from each other and there is not much chance to find them close together at small hyperradius. The three atoms cannot reach the region of configuration space where couplings to the other hyperspherical states is efficient. As for the bosonic system, inelastic processes are faster than the elastic ones at ultralow energy for the last vibrational state.

In our study, two features differ from the condensation experiments of diatomic molecules composed of fermionic atoms where elastic processes are faster than inelastic ones [1–4]. First, the depletion in inelastic rates for the last vibrational state of the molecule is present in both fermionic and bosonic systems, which confirms that it is not due to Pauli blocking. Second, according to the diatomic potential energy curves used in the present work, we find an atom-atom s-wave scattering length of $-26a_0$ for ^{7}Li$_2$ and an atom-atom p-wave scattering length of $-38a_0$ for ^{6}Li$_2$, which corresponds to a binding energy of 0.0864 meV (1 K) for ^{6}Li$_2$ $(v=9,\ j=1)$. For the fermionic system, this contrasts with the large and positive atom-atom scattering length of $3500a_0$ [2] obtained in molecular BEC experiments, suggesting that Pauli blocking does not occur when the atom-atom scattering length is small and negative. This confirms that the sign and the value of the atom-atom scattering length play an important role.

We find for the collisions in the bosonic lithium system that the inelastic rates show a strong and irregular dependence on the vibrational state of the molecule. However, recent measurements of inelastic rate coefficients for the bosonic Cs+Cs$_2$($^3\Sigma_u^+$) system [27,28] at ultracold temperatures did not show a dependence of rate coefficients on the vibrational state of the diatomic molecule.

Several reasons may be at the origin of this difference between the Li and Cs systems. A first reason may lie in the three-body part of the Li$_3$ interaction potential which is

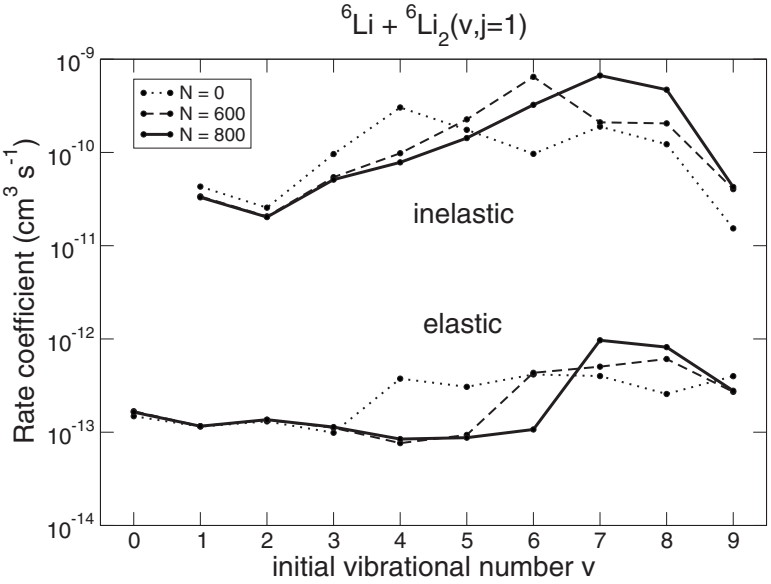


FIG. 3. Elastic and inelastic rate coefficients for ^{6}Li+^{6}Li$_2$ $(v,j=1)$ (fermionic isotopes) for $N=0$ (dotted curve), $N=600$ (dashed curve), and $N=800$ (bold solid curve), where N is the number of double-continuum states. The collision energy is 10^{-9} K.

strongly attractive and roughly one order of magnitude larger than for Cs_3 [29]. We calculated the rate coefficients for $^7Li+^7Li_2$ without the three-body term V_3. We see in Fig. 2 that, except for a sharp decrease at $v=2$, the inelastic rates increase more regularly and monotonically up to $v=9$ and are depleted for $v=10$ for the reason already pointed out above. For this state, the influence of the three-body term which is short ranged is not important while for the lowest vibrational states it is as in our previous study [9]. We obtain an inelastic rate which differs by only 3% for $v=10$ from the one obtained with the full potential. A second reason may lie in the temperature (~ 50 μK in the Cs experiments) which is high enough so that a few partial waves with nonzero orbital angular momentum l contribute to inelastic rate coefficients instead of only one ($l=0$) in the present calculations. Finally, the masses of the collision partners are very different. In previous work on the light $H+H_2$ system [25,26] with a small density of states, a large dependence of inelastic rates on the vibrational quantum number v has been found. When the density of states was increased by increasing the mass of the hydrogen atoms [26], the dependence of inelastic rates on v was much less important.

In conclusion, our work shows that vibrational deexcitation in $Li+Li_2$ is more efficient than elastic scattering at ultralow energies if the di-alkali-metal molecules formed from bosonic or fermionic atoms are in high vibrational states, especially in the highest, when the atom-atom scattering length is small and negative. This result is consistent with our previous studies on alkali-metal systems with di-alkali-metal molecules in low vibrational states. Our study also shows that a large number of hyperspherical double-continuum states are needed to describe accurately the dynamics for high vibrational states of the molecule. We find a strong and irregular dependence of the inelastic rates on v for the bosonic lithium system which is partly due to a very strong three-body potential.

The dynamical calculations reported in this paper have been performed with computer time provided by the "Institut du Développement des Ressources en Informatique Scientifique" (IDRIS, Orsay, France).

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