Elastic scattering of two ⁷Li atoms

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Interaction potentials for the $X\,{}^1\Sigma_g^+$ and $a\,{}^3\Sigma_u^+$ states of Li_2 are constructed and used in calculations of the elastic scattering of two ⁷Li atoms at ultralow temperatures. The extreme sensitivity of the cross sections to the details of the interaction potentials is demonstrated. The calculated elastic and spin-change cross sections are very large, of the order of 10^{-13} cm² at zero temperature. The predicted scattering length for the triplet state is negative with a value of $-17.2a_0$. Pronounced shape resonances appear at energies of 4.9×10^{-8} a.u. in the singlet scattering and 5.5×10^{-7} a.u. in the triplet scattering.

PACS number(s): 34.40.+n

I. INTRODUCTION

Collisions of alkali-metal atoms at ultralow temperatures have been studied recently in many experiments. The processes that occur at millidegrees Kelvin temperatures are sensitive to the details of the interaction potentials between the colliding systems over an extended range of internuclear distances. We explore here the simple case of the elastic scattering at near-zero temperatures of a pair of lithium atoms for which apparently accurate interaction potentials can be constructed. We show that nevertheless their precision is not sufficient for a reliable prediction of the elastic and spin-change cross sections, though it is likely that the cross sections are very large.

II. ELASTIC-SCATTERING THEORY

The theory of scattering by a potential $V(r)$, where r is the interatomic distance, is given in many textbooks. A partial-wave expansion reduces the problem to the determination of the solutions of the partial wave equation:

$$\frac{d^2 u_l}{dr^2} + \left\{ k^2 - \frac{2\mu V(r)}{\hbar^2} - \frac{l(l+1)}{r^2} \right\} u_l(r) = 0 , \quad (1)$$

where μ is the reduced mass of the collision system and k is the wave number given in terms of the energy E of relative motion by $k^2 = 2E\mu/\hbar^2$. The solutions must be regular and behave asymptotically as

$$u_l(r) \sim A_l \{ s_l(kr) + \tan\delta_l n_l(kr) \} , \quad (2)$$

where $s_l(r)$ and $n_l(r)$ are, respectively, the spherical Bessel and Neumann functions; A_l is an arbitrary amplitude, and δ_l is the scattering phase shift. Alternatively, we may write

$$u_l(r) \sim A_l \sin(kr - \tfrac{1}{2}l\pi + \delta_l) . \quad (3)$$

If A_l is chosen equal to unity, the solution $u_l(r)$ satisfies the integral equation

$$\tan\delta_l = \frac{-2\mu}{\hbar^2 k} \int_0^\infty s_l(kr) V(r) u_l(r) dr . \quad (4)$$

The scattering by $V(r)$ is described by the phase shifts δ_l and a total elastic cross section may be defined by

$$\sigma_{el}(E) = \frac{4\pi}{k^2} \sum_{l=0}^\infty (2l+1)\sin^2\delta_l . \quad (5)$$

For lithium atoms in their ground states, approach may occur along the potential-energy curves $V_g(r)$ and $V_u(r)$, corresponding, respectively, to the $X\,{}^1\Sigma_g^+$ and $a\,{}^3\Sigma_u^+$ states of Li_2. Elastic singlet and triplet cross sections may be defined by

$$\sigma_{el}^s = \frac{4\pi}{k^2} \sum_{l=0}^\infty (2l+1)\sin^2\delta_l^s , \quad (6)$$

$$\sigma_{el}^t = \frac{4\pi}{k^2} \sum_{l=0}^\infty (2l+1)\sin^2\delta_l^t , \quad (7)$$

and an elastic spin-change cross section may be defined by

$$\sigma_{sc} = \frac{\pi}{k^2} \sum_{l=0}^\infty (2l+1)\sin^2(\delta_l^s - \delta_l^t) . \quad (8)$$

At values of k close to zero, only the $l=0$ term in each of Eqs. (6), (7), and (8) contributes. The $l=0$ phase shift δ_0 can be represented by the effective range expansion [1]

$$k \cot\delta_0 = \frac{-1}{a} + \frac{1}{2} r_e k^2 - T k^4 + \cdots . \quad (9)$$

The parameter a is the scattering length and the parameter r_e is the effective range. In the limit of zero energy,

$$\sigma_{el}^s = 4\pi a_s^2, \quad \sigma_{el}^t = 4\pi a_t^2, \quad \sigma_{sc} = \pi(a_s - a_t)^2 , \quad (10)$$

where a_s and a_t are, respectively, the singlet and triplet scattering lengths. The scattering length corresponding to a potential $V(r)$ that decreases at large r as $-C_n/r^n$ has been obtained semiclassically by Gribakin and Flambaum [2] in the form

$$a = \bar{a} \left\{ 1 - \tan \left[\frac{\pi}{n-2} \right] \tan \left[\Phi - \frac{\pi}{2(n-2)} \right] \right\} , \quad (11)$$

where

$$\bar{a} = \cos \left[\frac{\pi}{n-2} \right] \left\{ \frac{(2\mu C_n)^{1/2}}{\hbar(n-2)} \right\}^{2/(n-2)} \frac{\Gamma \left[\frac{n-3}{n-2} \right]}{\Gamma \left[\frac{n-1}{n-2} \right]} \quad (12)$$

and

$$\Phi = \frac{1}{\hbar} \int_{r_0}^{\infty} \{ 2\mu [-V(r)] \}^{1/2} dr , \quad (13)$$

where $V(r_0) = 0$. Gribakin and Flambaum have also shown that the number of bound states n_b is given by

$$n_b = \left[\frac{\Phi}{\pi} - \frac{n-1}{2(n-2)} \right] + 1 , \quad (14)$$

where [ ] indicates the largest integer. When [ ] in Eq. (14) is an integer, the scattering length is infinite.

The effective range r_e can be expressed in terms of the zero-energy solutions of the partial-wave equation (1). If $\omega_0(r)$ is the solution of Eq. (1) at $k = 0$ with the potential taken to be zero everywhere, normalized so that

$$\omega_0(r) = \frac{\sin(kr + \delta_0)}{\sin\delta_0} , \quad (15)$$

and if $u_0(r)$ is normalized so that at large r,

$$u_0(r) \sim \omega_0(r) , \quad (16)$$

then [1,3]

$$r_e = 2 \int_0^{\infty} dr \{ \omega_0^2 - u_0^2 \} . \quad (17)$$

A more complicated expression may be written for the coefficient T in Eq. (9) [1].

If a bound state with binding energy $E_b = \hbar^2 \gamma^2 / 2\mu$ lies near to the dissociation limit within the domain of convergence of the effective range expansion, a and r_e are related by [3]

$$\frac{-1}{a} = -\gamma + \frac{1}{2} r_e \gamma^2 + \cdots . \quad (18)$$

III. INTERACTION POTENTIALS

The interaction potentials of two lithium atoms have been discussed by Zemke and Stwalley [4], and we followed broadly their recommendations, though with some modifications. Barakat et al. [5] have constructed an empirical Rydberg-Klein-Rees (RKR) potential-energy curve for the $X\,^1\Sigma_g^+$ state at internuclear distances between $3.4a_0$ and $23.9a_0$. (There are two misprints in the data. In their Table 4, $R_2(v=25)$ should read 4.890 860, not 4.490 860, and $R_2(v=31)$ should read 5.680 896, not 5.580 896.) We extended the data of Barakat et al. [5] by

using values from Konowalow and Olson [6] at $2.75a_0$ and $3.00a_0$ and a value of Schmidt-Mink, Müller, and Meyer [7] at $3.25a_0$.

At large separations, $V_g(r)$ and $V_u(r)$ may be written as a sum of dispersion terms r^{-n} and an exchange potential $V_{exc}(r)$ which diminishes exponentially. Thus, at large r,

$$V_{g,u}(r) = \frac{-C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} \mp V_{exc}(r) . \quad (19)$$

For C_6, C_8, and C_{10} we used the values of Marinescu, Sadeghpour, and Dalgarno [8]. They are compared in Table I with those adopted by Zemke and Stwalley [4]. Their value of C_{10} is an approximate estimate made using the empirical relationship $C_{10} = 1.3(C_8^2/C_6)$. The value we adopted is a recent theoretical prediction and should be more reliable.

The exchange term $V_{exc}(r)$ is very important to the determination of the spin-change cross section and special care is needed if the correct cross sections are to be obtained at low temperatures. Zemke and Stwalley [4] found that the form $A \exp(-\alpha r)$ is a very good approximation between $11a_0$ and $19a_0$, but it must become inadequate beyond this range, and Smirnov and Chibisov [9] have shown that if ρ^2 is the ionization potential of the atom in a.u., the exchange interaction has the asymptotic form

$$V_{exc}(r) = \tfrac{1}{2}(V_u - V_g) = Cr^{\alpha} \exp(-\beta r) , \quad (20)$$

where $\alpha = -1 + 7/2\gamma$, $\beta = 2\rho$, and C is a constant which can also be expressed as a function of ρ. We determined C by fitting (20) to $V_{exc}(r)$, matching $V_g(r)$ and $V_u(r)$ at the largest values of r for which they are reliably determined by experimental data, to obtain

$$V_{exc}(r) = 0.012\,88 r^{4.558} \exp(-1.259r) . \quad (21)$$

The experimental data on the $a\,^3\Sigma_u^+$ state over a less extensive range of r. We used the RKR values of Linton et al. [10] between $6.4a_0$ and $15.7a_0$, and we added theoretical values at $3.00a_0$ from Konowalow, Regan, and Rosenkrantz [11] and between $3.25a_0$ and $6.00a_0$ from Schmidt-Mink, Müller, and Meyer [7]. The long-range form is the same as for $V_g(r)$, except the exchange term is repulsive.

Our adopted potentials yield a value of 8516.618 cm^{-1} for the dissociation energy of the $X\,^1\Sigma_g^+$ state in close agreement with the value of 8516.78 cm^{-1} of Barakat et al. [5] and 8516.61 cm^{-1} of Zemke and Stwalley [4], and a value of 333.396 cm^{-1} for the dissociation energy of the $a\,^3\Sigma_u^+$ state in close agreement with the values of 333 cm^{-1} of Lindton et al. [10] and 333.4 cm^{-1} of Zemke and Stwalley [4].

A second set of potentials was used to demonstrate the

TABLE I. Long-range coefficients in Eq. (19) in a.u.

Ref.	C_6	C_8	C_{10}
[4]	1381	82 616	6 425 000
[8]	1388	83 230	7 348 000

0.30

0.25

0.20

0.15

V(r) (a.u.)

0.10

0.05

0

-0.05

0   5   10   15   20
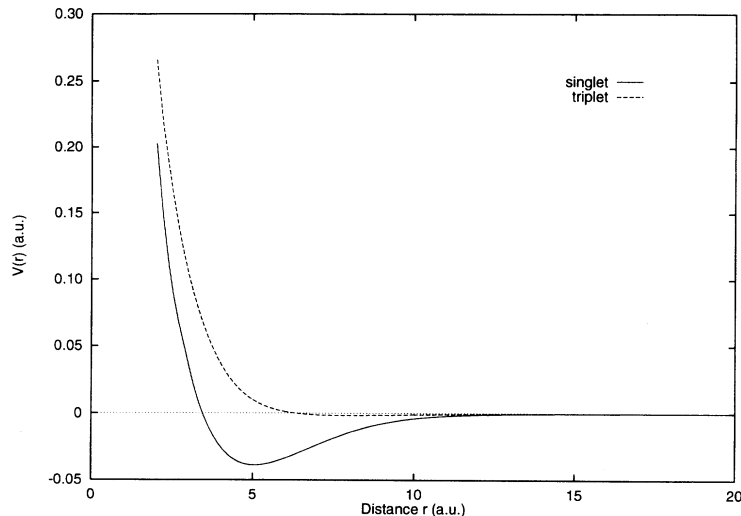
Distance r (a.u.)

singlet ——
triplet ----

FIG. 1. The adopted potential-energy curves of the $X\,^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ states of Li$_2$.

sensitivity of the cross sections. For $V_g(r)$ and $V_u(r)$, we used the ab initio calculations and the long-range extrapolation of Konowalow and Fish [12], Konowalow and Olson [6], and Konowalow, Regan, and Rosenkrantz [11], which has the form

$$V_{g,u}(r)=\frac{-1390}{r^6}-\frac{12\times10^5}{r^8}\mp46.5\exp(-0.997r)\ .$$

(22)

There is a small discrete step in the data which we smoothed.

The adopted hybrid potential curves of the singlet and triplet states are illustrated in Fig. 1. The differences between the two sets of singlet potentials and the differences between the two sets of triplet potentials are too small to be shown in Fig. 1.

IV. ZERO-ENERGY LIMIT

We solved Eq. (1) by the Numerov method. We found that a more stable phase is obtained at low energies by substituting the solution into the integral equation (4) [13], rather than by fitting to the asymptotic form. We determined the scattering lengths and effective ranges by fitting the scattering phase shift $\delta_0(k)$ to the effective range formula (9). We also calculated the scattering lengths using Eq. (11) and the effective ranges using Eq. (17). We adopted an atomic mass of 7.016 003 g/mole and a reduced mass of 6394.6955 electron masses, corresponding to the collision of ^{7}Li and ^{7}Li.

The scattering lengths and effective ranges for the $X\,^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ potentials are presented in Table II. The close agreement between the calculations of a from Eqs. (9) and (11) and of r_e from Eqs. (9) and (17) confirms the accuracy of the numerical integrations of the partial-wave equation (1). The negative triplet scattering length suggests the existence of a bound state close to the continuum edge [3].

The scattering lengths corresponding to the alternative

potential-energy curves for the $X\,^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ states are, respectively, $-0.2a_0$ and $1720a_0$, values that are quite different in magnitude and sign from those in Table II which correspond to our adopted hybrid potential curves. The remarkable sensitivity of the scattering lengths to the details of the potential-energy curves may be anticipated by inspection of Eqs. (11) and (14) or Eq. (18) which, consistent with Levinson's theorem, show that as the binding energy of the highest levels tends to zero, the magnitude of the scattering length tends to infinity.

We have obtained the binding energies of the vibrational levels with zero angular momentum. They are listed in Table III for the highest-lying levels, together with the experimental data [5,10]. We found 42 bound levels for the $X^1\Sigma_g^+$ state and 11 bound levels for the $a\,^3\Sigma_u^+$ states. We confirmed that we had discovered all the bound levels by calculating the total number for each potential using the formula (14) of Gribakin and Flambaum [2]. Further confirmation was obtained by slightly modifying an analysis of LeRoy and Bernstein [14], who used semiclassical arguments to derive for the binding energy E_v of vibrational level v in a potential Cr^{-n} the expression

$$E(v)=[(v_D-v)H_n]^{2n/(n-2)}\ ,$$

(23)

where v_D is the effective vibrational noninteger quantum number of the dissociation limit and

TABLE II. Scattering length a and effective ranges r_e in units of a_0.

State	a		r_e	
	Eq. (9)	Eq. (11)	Eq. (9)	Eq. (17)
$X\,^1\Sigma_g^+$	36.9	36.9	66±1	66.5
$a\,^3\Sigma_u^+$	−17.2	−16.9	1012±4	1014.8

TABLE III. Energies of the $X\,^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ vibrational levels in cm^{-1}.

	$X\,^1\Sigma_g^+$			$a\,^3\Sigma_u^+$	
v	Experiment	Theory	v	Experiment	Theory
33	8205.232	8205.156	2	142.637	142.577
34	8292.029	8291.967	3	188.358	188.329
35	8364.307	8364.235	4	227.803	227.752
36	8421.613	8421.589	5	260.958	260.885
37	8463.965	8463.967	6	287.779	287.723
38	8492.044	8492.110	7	308.229	308.199
39	8507.842	8507.940	8		322.134
40	8514.778	8514.803	9		330.001
41		8516.541	10		333.014

$$H_n = \left[\frac{n-2}{2n}\right]^{\hbar}\left[\frac{2\pi}{\mu}\right]^{1/2}\frac{\Gamma\left[1+\dfrac{1}{n}\right]}{\Gamma\left[\dfrac{1}{2}+\dfrac{1}{n}\right]}\frac{n}{C^{1/n}}\,. \qquad (24)$$

The total number of vibrational levels is the greatest integer less than or equal to $v_D + 1$. The parameter n and the value of C are determined by the value of the interaction potential at the outer turning point $R(v^*)$ of the chosen bound level v^*. Thus,

$$n+1 = \frac{\sum(m+1)mC_m/R(v^*)^{m+1}}{\sum mC_m/R(v^*)^{m+1}}\,, \qquad (25)$$

where the summation is taken over $m = 6$, 8, and 10 and

$$E(v^*) = C/R(v^*)^n \qquad (26)$$

defines C. Then,

$$v_D = v + \frac{[E(v)]^{(n-2)/2n}}{H_n}\,. \qquad (27)$$

Table IV lists the results for the $X^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ states obtained using in Eqs. (25) and (26) vibrational level $v^* = 40$ for the $X\,^1\Sigma_g^+$ state and 7 for the $a\,^3\Sigma_u^+$ state and applying (27) to several of the highest-lying vibrational levels. All yield 42 levels for the $X\,^1\Sigma_g^+$ state and 11 for the $a\,^3\Sigma_u^+$ state.

The binding energies of the highest bound levels correspond to values of γ of 0.0667 and 0.149 a.u., respective-

ly, for the singlet and triplet states. The scattering lengths derived using Eq. (18) are not useful estimates because γr_e is large compared to unity and neither value of γ is within the domain of convergence of Eq. (18).

Calculations of the triplet scattering length for $^7\mathrm{Li}$ atoms have been reported recently by Moerdijk et al. [15]. Taking account of uncertainties in the $a\,^3\Sigma_u^+$ interaction potential, they conclude that

$$-27.8a_0 < a < -7.1a_0\,.$$

Our value is $-17.2a_0$.

V. HIGHER PARTIAL WAVES

With increasing energy, higher angular momentum waves contribute to the scattering. Figure 2 illustrates the variation with energy of the individual partial-wave cross sections for the $X\,^1\Sigma_g^+$ state. The total elastic cross section in units of a_0^2 is also presented in Fig. 2. The total cross section is constant at low velocities where only s-wave scattering is significant. The s-wave cross section tends to decrease with increasing energy but the decrease is overcome by the higher partial-wave contributions which initially increase with energy from zero before passing through maxima and decreasing. Oscillations occur through the addition of a small number of partial waves. Sharper structures are due to shape resonances. The most prominent is the d-wave resonance corresponding to a quasi-bound-state trapped by the $l = 2$ centrifugal barrier. The d-wave resonance occurs at an energy of 4.9×10^{-8} a.u. and has a width of 1.5×10^{-8} a.u.

TABLE IV. Parameters of the LeRoy-Bernstein method.

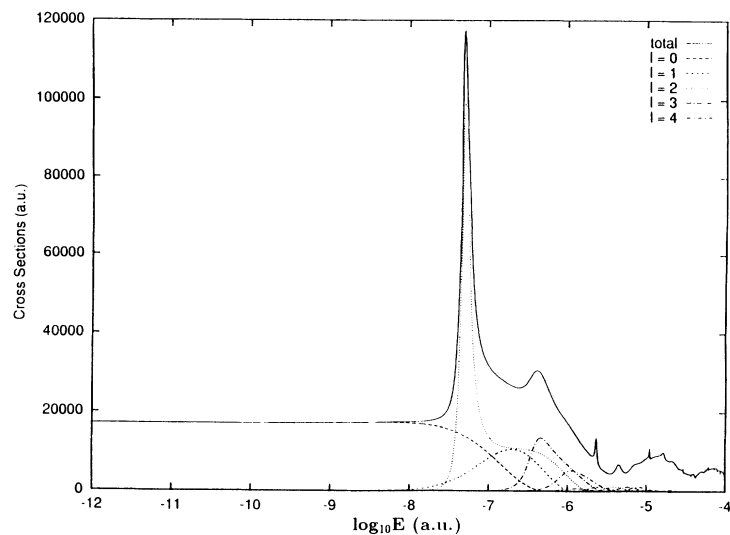| State	v^*	n	C (a.u.)	v	v_D
$X\,^1\Sigma_g^+$	40	6.333	4409	39	41.549
				40	41.492
				41	41.505
$a\,^3\Sigma_u^+$	7	6.839	17 184	6	10.074
				7	10.301
				8	10.482
				9	10.624
				10	10.750

FIG. 2. The individual partial-wave cross sections and the total cross section for scattering in the $X\,^1\Sigma_g^+$ state as functions of collision energy.
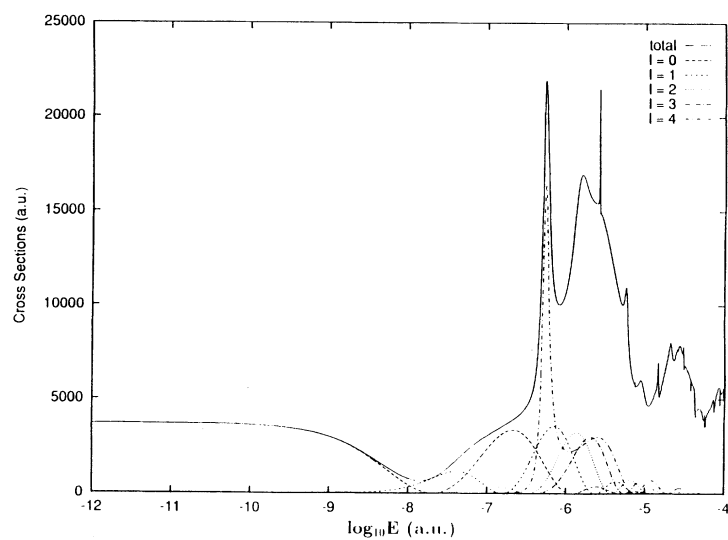
FIG. 3. The individual partial-wave cross sections and the total cross section for scattering in the $a\,^3\Sigma_u^+$ state as functions of collision energy.
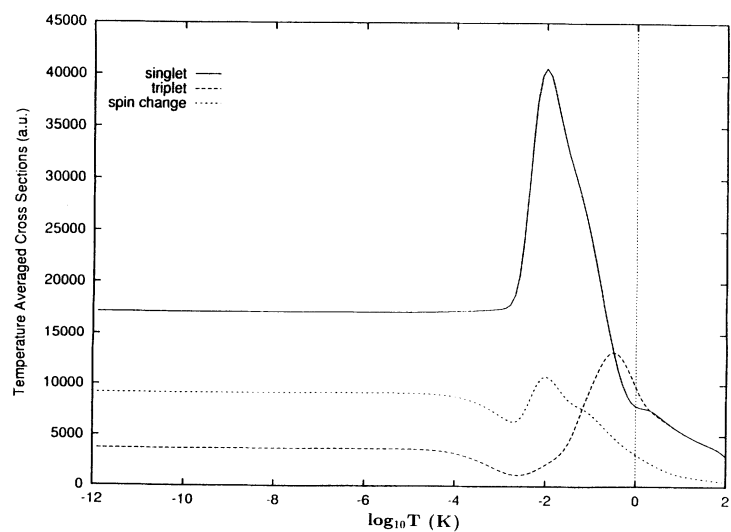
FIG. 4. The thermally averaged elastic and spin-change cross sections as functions of temperature.

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TABLE V. Spin-change rate coefficients calculated using the cross section defined in Eq. (8).

$\log_{10}$ [T (K)]	k (cm^{3}s^{-1})
-6	2.0 (-12)
-5	6.3 (-12)
-4	1.9 (-11)
-3	4.8 (-11)
-2	2.4 (-10)
-1	4.9 (-10)
0	6.9 (-10)
1	7.7 (-10)
2	9.9 (-10)

We illustrate in Fig. 3 the similar calculations for the $a\,^3\Sigma_u^+$ state. A strong resonance appears in the $l=4$ partial wave at an energy of 5.5×10^{-7} a.u. with a width of 1.3×10^{-7} a.u.

VI. TEMPERATURE DEPENDENCE

We assume the velocity distribution is Maxwellian characterized by a kinetic temperature T, and we define mean elastic and spin-charge cross sections by

$$\bar{\sigma}(T)=(k_BT)^{-2}\int_0^\infty \sigma(E)E\exp(-E/k_BT)dE \ . \quad (28)$$

The corresponding rate coefficients are given by $(8k_BT/\pi\mu)^{1/2}\bar{\sigma}(T)$.

Values of the mean cross sections in units of a_0^2 are shown in Fig. 4 for T up to 10 K and values of the spin-change rate coefficient in cm^{3}s^{-1} are listed in Table V for T up to 100 K. The cross sections are large and, because of the sensitivity to the details of the interaction potential, they are very uncertain at low temperatures. At higher temperatures where many partial waves contribute, the predictions are more reliable. The influence of higher partial waves begins to become evident at temperatures as low as 10 mK.

VII. CONCLUSIONS

The elastic cross sections for the collision of two ^{7}Li atoms at ultralow temperatures are sensitive to the details of the interaction potentials but are probably very large, of the order of 10^{-13} cm^2. Below 10 mK, the collisions are dominated by s-wave scattering, but higher-order partial waves contribute at higher temperatures. Shape resonances, trapped within the centrifugal barrier, impose structure on the cross sections. The scattering lengths are predicted to be positive for singlet scattering and negative for triplet scattering.

ACKNOWLEDGMENTS

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