Exoergic Collisions of Cold Na*-Na

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We calculate rates for two exothermic excited-state collision processes involving sodium at ultracold temperatures. We predict that the rate for fine-structure changing collisions exceeds that of radiative redistribution with release of enough energy to cause loss from current optical traps. A semiclassical treatment is used which accounts for the frequency dependence of absorption and spontaneous emission in midcollision

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Recent observations of collisions between trapped atoms [1-4] have opened the field of ultracold collisions to experimental study. Many novel features result from a 10^6 reduction of usual thermal energies: long de Broglie wavelength λ_D, predominance of *s*- and *p*-wave scattering, importance of weak (e.g., magnetic dipole-dipole) forces, and long collision duration (e.g., not sudden with respect to hyperfine interaction times). These have been noted by many authors,[5-10] who also agree that the most challenging new physics arises in collisions of excited atoms, due to the high probability of spontaneous decay during the collisions. In these slow, long-range encounters the probability of absorption, stimulated, and spontaneous radiative transitions can approach unity; consequently, radiation may no longer be treated as a perturbation on the collision dynamics—even in weak radiation fields.

We now present a semiclassical treatment of excited-state collisions in which nuclear motion on the (undressed) molecular potentials is treated classically, affording a clear conceptual picture of the effects of spontaneous emission during the collision. We have restricted our attention to two processes involving one excited- and one ground-state atom which can impart enough kinetic energy to expel atoms from current atom traps (∼1 K of energy): fine-structure changing collisions and radiative redistribution.

The first is the familiar fine-structure changing process,

$$\mathrm{Na}+\mathrm{Na}+\hbar\omega\rightarrow \mathrm{Na}_2^*(3P_{3/2})$$
$$\rightarrow \mathrm{Na}^*(3P_{1/2})+\mathrm{Na}+\Delta E_{\mathrm{FS}}\,, \qquad (1)$$

where the $\mathrm{Na}_2^*(3P_{3/2})$ represents a long-range molecule (in Hund's case *c*). This process transfers $\Delta E_{\mathrm{FS}}/2\cong 12$ K to nuclear kinetic energy of each atom, causing both to escape from the trap. The second mechanism,

$$\mathrm{Na}+\mathrm{Na}+\hbar\omega\rightarrow \mathrm{Na}_2^*\rightarrow \mathrm{Na}+\mathrm{Na}+\hbar\omega'\,, \qquad (2)$$

is known as radiative redistribution.[11,12] It transfers $\hbar(\omega-\omega')/2$ to each atom, as shown diagrammatically in the inset portion of Fig. 1. The latter mechanism has already been suggested as a heating mechanism,[7,8] but not calculated. Quantum corrections are discussed; they are not expected to cause major changes in our predictions.

A molecular viewpoint is necessary in order to treat radiative phenomena that occur at internuclear separations $R<\lambda\!\!\!^{-}_{\mathrm{light}}$. Half of the Na*-Na molecular states have dipole-forbidden transitions to the ground state, the other half are dipole allowed with spontaneous decay rate $\Gamma_M=2\Gamma_A=1.2\times10^8\ \mathrm{s}^{-1}$, where Γ_A is the atomic rate. Neglecting hfs, there are ten distinguishable long-range $\mathrm{Na}^*(2P_{3/2})$-Na adiabatic potentials, which are equally positive and negative interactions and radiating

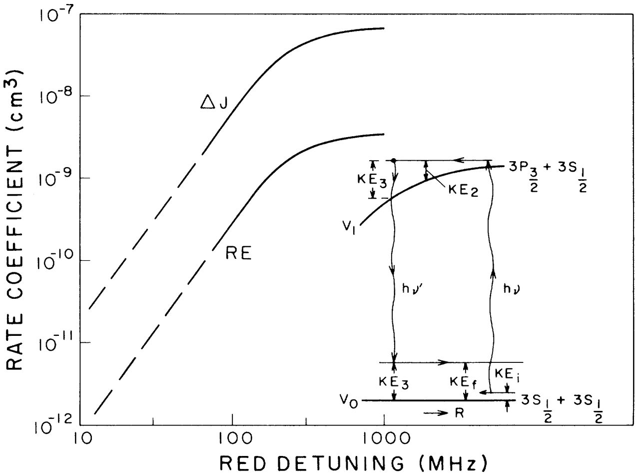

FIG. 1. Rate coefficients vs red detuning Δ for $3P_{3/2}\rightarrow 3P_{1/2}$ excitation transfer for $P_J=0.2$ (labeled Δ*J*) and radiative escape (RE). Inset: radiative redistribution. A ground-state pair approaches with kinetic energy KE_i, which is conserved during photoexcitation but increases to KE_2 and KE_3 as the Na*-Na pair separation decreases. This KE_3 is preserved during spontaneous emission, resulting in trap escape by both Na atoms if ω′ is sufficiently red.

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and nonradiating states.[13] The collisions under consideration here are dominated by absorption to potential curves of attractive, radiating states of the Na*$(3P_{3/2})$-Na pair at $R \leq 500$ Å, and motion from there into the few Å region.

The dominant molecular interaction in this region is the long-range electrostatic dipole-dipole interaction which we represent as $\pm \bar{C}R^{-3}$ for the repulsive and attractive states, $\bar{C}=8.4$ a.u. being the average coefficient of all the potential curves dissociating to $3S+3P_{3/2}$. For $R<500$ Å, $\bar{C}R^{-3}$ exceeds the excited-state hyperfine interaction, so we are justified in neglecting the complications of hyperfine recoupling (which occurs in the region labeled ΔF in Fig. 2).

Our calculation begins with "stationary" ground-state atom pairs at internuclear separation R_0. The semiclassical excitation rate $\mathcal{R}$ for exciting this pair to the attractive $(-\bar{C}R^{-3})$ state is

$$\mathcal{R}(R_0,\omega_L,I)=\left[\frac{(\Gamma_M/2)^2}{[\omega_L-\omega(R_0)]^2+(\Gamma_M/2)^2}\right]\frac{I}{\hbar\omega_L}\frac{\lambda^2}{2\pi}$$
$$=\epsilon(\omega_L,R_0)\frac{I}{\hbar\omega_L}\frac{\lambda^2}{2\pi}. \qquad (3)$$

Here $\omega(R_0)=\omega_0-\bar{C}R_0^3/\hbar$ is the molecular resonant absorption frequency, ω_L and I are the laser beam frequency and intensity, ω_0 is the atomic resonant frequency, and the cross section $\lambda^2/2\pi$ is $\frac{1}{2}$ of the atomic $(3S_{1/2}\text{-}3P_{3/2})$ value, for the attractive state. $\epsilon(\omega_L,R_0)$ is shown in Fig. 2 to show the R_0 regions excited by various detunings; for 10 and 30 MHz this does not include hfs, hence is only indicative of the general R_0 region.

Stimulated emission and the concomitant saturation are omitted from Eq. (3) since our primary objective is to study the effects of spontaneous emission on low-intensity processes. Power broadening and stimulated emission may be expected[6] to greatly modify the collision dynamics at relatively low intensities (W/cm^2), in contrast to thermal collisions where they are important only at extremely high intensities (MW/cm^2).[14]

After excitation at R_0, the excited-atom pair is drawn together by the $-\bar{C}R^{-3}$ interaction, reaching the $R<60$ Å region where trap-loss processes can occur in essentially the same time $t(R_0)$ as that for reaching $R=0$ in a pure $-\bar{C}R^{-3}$ interaction, i.e.,

$$t(R_0)=1.4\left(\frac{\mu}{2}\right)^{1/2}\int_0^{R_0}dR\left(\frac{\bar{C}}{R^3}-\frac{\bar{C}}{R_0^3}\right)^{-1/2}$$
$$=\left(\frac{\mu R_0^5}{2\bar{C}}\right)^{1/2}=\left(\frac{\Delta_\tau}{\Delta}\right)^{5/6}\Gamma_M^{-1}, \qquad (4)$$

where μ is the reduced mass, $\Delta=\omega_0-\omega_L$ is the detuning, $\Delta_\tau=240$ MHz is the detuning corresponding to $R_0=R_\tau=330$ Å, where $t(R_\tau)=\Gamma_M^{-1}$ (see Fig. 2). Equation (4) without the factor of 1.4 applies to initially stationary atoms; we found that this factor compensates approximately for the effects of initial thermal motion when $kT<\bar{C}R_0^{-3}$.

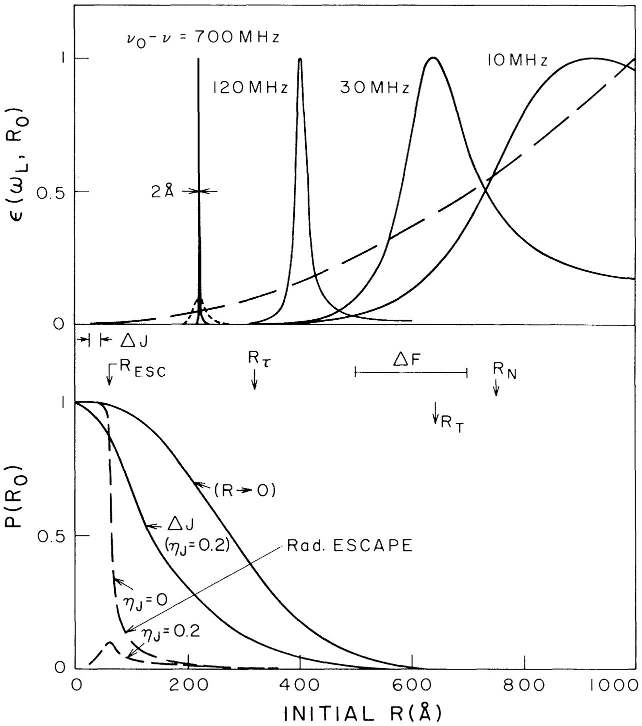

FIG. 2. Contributions to the integrand of Eq. (5). Top: $\epsilon(\omega_L,R_0)$, the relative absorption coefficient of Na*-Na pairs, vs R_0 for several values of red detuning. The long-dashed line is the R_0^2 factor, and the short-dashed line indicates the broadening discussed in the text. Bottom: Probability β of reaching the small-R region from R_0 before radiative decay (labeled $R\rightarrow 0$), and of undergoing a ΔJ process before spontaneous emission (labeled ΔJ). Dashed curves show probabilities of radiative escape (RE) assuming $\eta_J=0$ and 0.2.

Although λ_D is long (~50 Å for Na-Na at 1 mK), this semiclassical absorption followed by classical motion is justified as follows. The significant R_0 region is 300 to 500 Å, so that several partial waves are required to describe the nuclear motion—consequently, quantum oscillations largely average out. The excited vibrational levels of importance are closer than Γ_M so a coherent superposition is excited, producing an inward-moving wave packet whose initial spatial extent $(\sim 0.1R_0)$ is smaller than the ground-state λ_D. The semiclassical absorption is thus broadened by the finite excited-state nuclear wavelength, but since the integrated absorption is preserved and this has only a minor effect on the continuum absorption coefficient, as utilized here. However, it does raise the saturation intensity (e.g., by ~20× at 1-GHz detuning). An example of this broadening is shown in Fig. 2 as a dashed line at 700-MHz detuning. At large detunings the continuous absorption coefficient is replaced by a bound molecular spectrum of lines Γ_M

wide. (The possibility of high-resolution free-bound spectroscopy has been noted before.[5,8]) As there are actually several different molecular potentials, each with hfs and rotational structure, this spectrum may not be resolvable until $\Delta > 1$ GHz.

The density of Na-Na pairs with separation $R_0 \rightarrow R_0 + dR_0$ is $[\mathrm{Na}]^2(4\pi R_0^2 dR_0)/2$. The probability that an Na*-Na pair undergoes a ΔJ transition before spontaneous emission will be labeled $P_{\Delta J}(R_0)$. The total rate $R_{\Delta}J$ of fine-structure transfers, per unit volume, is thus

$$R_{\Delta J} = \frac{[\mathrm{Na}]^2}{2} \int_0^{\infty} dR_0 4\pi R_0^2 \mathcal{R}(R_0, \omega_L, I) P_{\Delta J}(R_0) . \tag{5}$$

If the Na*-Na pair reaches the ($\sim$30 Å) J-recoupling region before radiating, it rapidly traverses this twice to yield a net J-changing probability η_J, equal to $2P(1-P)$ in the Landau-Zener approximation,[15] where P is the single-transit hopping probability. The probability of reaching this small-R region before spontaneous emission is $\beta = \exp[-\Gamma_M \Delta t(R_0)] = \exp[-(\Delta\tau/\Delta)^{5/6}]$ from Eq. (4). For the $R_0 \leq 500$ Å region of importance, the Na*-Na pair is trapped in the attractive $-C/R^3$ potential and will repeatedly traverse out to R_0 and back to $R \sim 0$ until radiating or undergoing a ΔJ transition (transfer between adiabatic states connected adiabatically to $3P_{3/2}$ can also occur, but will not greatly alter the following result). Thus

$$P_{\Delta J}(R_0) = \eta_J \beta + \eta_J (1-\eta_J)\beta^3 + \cdots$$
$$= \frac{\eta_J \beta}{1 - \beta^2 + \eta_J \beta^2} . \tag{6}$$

A rate coefficient $k_{\Delta J}$ for the ΔJ process is normally defined from the collision rate by

$$R_{\Delta J} = [\mathrm{Na}][\mathrm{Na}^*(3P_{3/2})] k_{\Delta J} . \tag{7}$$

The excited-atom density is dominated by free-atom excitation, so

$$[\mathrm{Na}^*(3P_{3/2})]\Gamma_A = (I_v/\hbar\omega_L)[\mathrm{Na}](\lambda^2/\pi)[1 + (2\Delta/\Gamma_A)^2]^{-1} . \tag{8}$$

Combining (3), (5), (7), and (8) yields

$$k_{\Delta J}(\omega_L) = \frac{\Gamma_A}{2} \left[\frac{(\Gamma_A/2)^2 + \Delta^2}{(\Gamma_A/2)^2} \right] \int_0^{\infty} dR_0 4\pi R_0^2 \epsilon(\omega_L, R_0) P_{\Delta J}(R_0) . \tag{9}$$

As ω_L is tuned into the red wing the integral in Eq. (9) increases; hence $k_{\Delta J}$ increases rapidly due to the Δ^2 factor. As ω_L is tuned into the blue wing the integral decreases as $\sim \Delta^{-2}$ and $k_{\Delta J} \sim$const.

The factors $\epsilon(\omega_L, R_0)$, $4\pi R_0^2$, and $P_{\Delta J}(R_0)$ in the integrand of Eq. (9) are shown in Fig. 2. The $k_{\Delta J}(\omega_L)$ that result from Eq. (9) are shown in Fig. 1. As noted previously, for $\Delta < 100$ MHz these results are only indicative as hfs has not been included. For the larger Δ values $\epsilon(R_0, \omega_L)$ is sharply peaked at $R = R_v$, where $\omega_L = \omega_0 - \bar{C}/\hbar R_v^3$. The integral in Eq. (9) reduces to $(4\pi R_v^2/|dv/dR|_{R_v})\{\Gamma_M/4\} P_{\Delta J}(R_v)$ by substitution of $dR_0 = dv/|dv/dR|_{R_v}$; the factor in parentheses is the quasistatic absorption coefficient. As can be seen by comparing the dashed line ϵ and $P_{\Delta J}$ in Fig. 2 the quantum spreading has only a minor effect on $k_{\Delta J}(\omega_L)$.

The rate coefficient k_{RE} for "radiative-escape" process (2) is given by Eq. (9) when $P_{\mathrm{RE}}(R_0)$ is substituted for $P_{\Delta J}(R_0)$. Here $P_{\mathrm{RE}}(R_0)$ is the probability of radiative emission at $R \leq R_E = 55$ Å during a transit through the $R \sim 0$ region; this will release at least 1-K kinetic energy causing both atoms to escape from current light traps. $P_{\mathrm{RE}}(R_0)$ is shown in Fig. 2, and was obtained as follows. For $R_0 > 140$ Å one must sum the results of multiple crossing, as in Eq. (6), where the probability of radiative escape is the radiative rate times the time spent at $R < R_E$, which we call $2t_E(R_0)$:

$$P_{\mathrm{RE}}(R_0) = 2t_E(R_0)\Gamma_m[\beta - (1-\eta_j)\beta^3 + \cdots] = \frac{2t_E(R_0)\Gamma_m \beta}{1 - \beta^2 + \eta_j \beta^2} . \tag{10}$$

In this R_0 region t_E is essentially independent of R_0 (the speed at R_E is dominated by the energy $\bar{C}_3 R_E^{-3}$) and $2t_E(R_0)R_m \approx 0.01$. For $R_0 < 140$ Å many oscillations occur [because $t(T_0)R_m \ll 1$] and the competition between radiative escape and j changing must be properly addressed. j-changing collisions occur at a rate $R_j = \eta_j/2t(R_0)$ and compete with radiative decay with the rate R_m. Of the radiative decays, a fraction $f_E = t_E/t(R_0) \cong (R_E/R_0)^{5/2}$ leads to radiative escape so $P_{\mathrm{RE}} = f_E \Gamma_m/(\Gamma_m + \Gamma_j)$. Obviously f_E is unity for $R_0 \lesssim R_E$. The $k_{\mathrm{RE}}(\Delta)$ that result are shown in Fig. 1.

Equation (10) applies for $\Delta < 3$ GHz, where comparison with Eq. (6) shows that $P_{\Delta J}(\Delta)/P_{\mathrm{RE}}(\Delta) = k_{\Delta J}(\Delta)/k_{\mathrm{RE}}(\Delta) = 100\eta_J$. The total trap-loss rate coefficient equals $2(1+100\eta_J)k_{\mathrm{RE}}$, where the factor of 2 results from two atoms ejected per ΔJ or radiative-escape collision. We estimate η_J by comparing the Landau-Zener adiabaticity parameter $[\alpha = v_{12}^2/\hbar(\dot{V}_{11} - \dot{V}_{22})]$ in the J-recoupling region to that of $\sim$350-K collisions of K*-K, Rb*-Rb, and Cs*-Cs. If one assumes the initially cold Na*-Na pairs have gained $\sim$8 cm^{-1} of kinetic energy before traversing the $\sim$30-Å recoupling region, their α falls between that of K*-K and Rb*-Rb. Interpolating between measured cross sections[16] yields $\eta_J \sim 0.2$ for this $T \cong 0$ K, Na*-Na case.

We draw several conclusions from these calculations. (1) Collisional trap loss should increase rapidly with red detuning (Fig. 1). A similar conclusion was reached for associative ionization by Na*-Na* collisions in traps.[6] (2) Fine-structure transfer is the dominant collisional trap-loss mechanism for $3P_{3/2}$ state excitation. (3) $k_{\Delta J}$ and k_{RE} are essentially independent of temperature below ~ 1 mK, because $\bar{C}/R_0^3$ greatly exceeds kT in the $R_0 < 400$ Å region of significance. (4) Spontaneous decay of Na*-Na pairs excited at $R_0 > 400$ Å occurs before the atoms are close enough for trap loss to occur, even though the normal Langevin process would draw Na*-Na pairs together from much larger range (~ 900 Å for $T = 1$ mK). (5) $k_{\Delta J}$ calculated here are large enough to explain the rate of collisional trap loss observed by Raab *et al.*,[2] but not the reported insensitivity to the fraction of Na*.

Up to this point we have assumed that the pair-distribution function of Na atom pairs is uniform. This is not justified for atoms that are frequently excited, as in current light traps. These move so slowly ($\sim 0.3 R_\tau$ in Γ_A^{-1}) that as little as 10% of saturation intensity will perturb the pair-distribution function at distances up to $\sim 10^3$ Å. Also, the spatial orientation of the atom-pair relative to the local radiation field direction causes preferential, successive excitation to attractive or repulsive excited states. This issue is beyond the scope of the present paper.

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