PHYSICAL REVIEW A, VOLUME 63, 021401(R)

Angular-momentum-state distribution of sodium atoms photoassociated in a magneto-optical trap

James P. Shaffer, Witek Chalupczak, and N. P. Bigelow
Department of Physics and Astronomy and The Laboratory for Laser Energetics, The University of Rochester, Rochester, New York 14627

(Received 27 May 1999; revised manuscript received 19 June 2000; published 5 January 2001)

We present direct spectroscopic measurement of the excited state angular-momentum-state distribution of $Na_2^*(3\,^2S_{1/2}+3\,^2P_{3/2})$ molecules photoassociated by the trapping lasers in a sodium magneto-optical trap. We find that states with quantum numbers up to $J=22$ are excited and that the measured population distribution can be well described using a local equilibrium model.

DOI: 10.1103/PhysRevA.63.021401 PACS number(s): 32.80.Pj, 03.75.Fi, 05.30.Jp

The study of ultracold collisions between ground- and excited-state atoms has received a great deal of attention [1]. Trap-loss measurements have revealed hyperfine- [2] and fine-structure-changing collisions [3], the rich detail of ultracold photoassociative spectroscopy has provided important information about long-range atom-atom interaction potentials [4], and intensity and time-resolved studies have provided insight into the kinetics and dynamics displayed by the atoms during the collision. One important issue is the complicated behavior of the near dissociation limit (long-range) photoassociation process that represents the common starting point of all optical cold collisions that occur in a magneto-optical trap (MOT) [6]. Recently, novel experiments have indicated that photoexcitation at long range, followed by spontaneous emission and reexcitation, still at long range, can enhance the relative approach velocity of the collision partners [5] (in the context of cold collisions, this excitation-decay-excitation cycle is referred to as recycling). In a related experiment [7], spectroscopy of ground-state molecules formed via photoassociation offered support for this picture. In this paper we present direct spectroscopic evidence that when two atoms colliding in a MOT are photoassociated, a relatively large number of angular-momentum states are populated.

In a recent paper [8], we described our use of resonantly enhanced multiphoton ionization (REMPI) to study Na_2 molecules excited in states that connect to the $3\,^2S_{1/2}+3\,^2D_{1/2-3/2}$ asymptote. To summarize: the excitation process was a 2+1 REMPI scheme [8] that began when a trapping laser photon was absorbed by a colliding atom pair, thus photoassociating the atoms into a molecular state at long range, near the $3\,^2S_{1/2}+3\,^2P_{3/2}$ asymptote [9] (see Fig. 1). Next, a photon from a separate tunable probe laser was absorbed. The probe laser was tuned to the red of the $3\,^2P_{3/2}\rightarrow 3\,^2D_{1/2-3/2}$ Na atomic transition at $\lambda=819$ nm. Population was transferred at the inner turning point of the singly excited Hund's case (a) $1\,^1\Pi_g$ and $1\,^3\Pi_u$ ($\Omega=0^+$ component) states into the $2\,^1\Pi_u$ and $2\,^3\Pi_g$ high-lying states. Subsequently, either a trap or probe photon was absorbed and $2\,^1\Pi_u$ or $2\,^3\Pi_g$ was ionized [8]. By analyzing the structure of the ion production spectrum as a function of the probe-laser detuning, we were able to extract precise molecular constants for the $2\,^1\Pi_u$ and $2\,^3\Pi_g$ states, and accurately deperturb the spectrum.

In the present work we consider the same experimental situation, but instead of using the REMPI spectrum as a tool to characterize the high-lying molecular potentials, we use it to study the angular-momentum-state populations present in the Na_2 intermediate-state quasimolecules formed in the initial photoassociation event. In our analysis, we take advantage of the fact that the amplitudes of the different lines observed in the ion spectra are governed by the angular-momentum states populated in the intial photoassociation by the trap light. We analyze the measured population distribution using a local equilibrium (LE) model [6,10] and find very good agreement with the observed rotational line amplitudes.

Our experiments were carried out in a vapor cell Na magneto-optical trap (MOT) [11,12]. The apparatus has been described in detail elsewhere [8]. Briefly, our sample consists of approximately 10^7 atoms at a density of $\sim 10^{10}$ cm^{-3} and a temperature at or near the Doppler temperature $T_D=240$ μK, as determined using a release-and-recapture method. The ion rate was measured with a time-of-flight

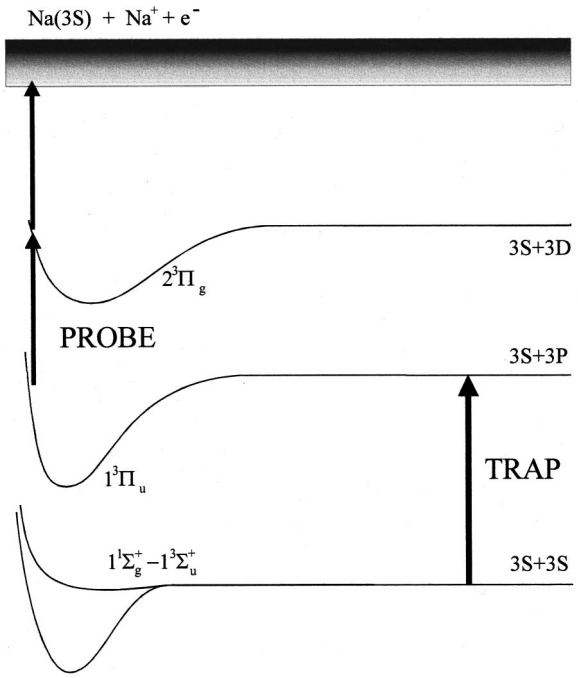

FIG. 1. The 2+1 REMPI excitation diagram for the experiment.

channel electron multiplier system. For compactness we do not reproduce our previously published detailed REMPI spectra here, but emphasize that the data used in the present work are the amplitudes of the lines assigned within the $2\,^3\Pi_g$ rotational spectrum.

To introduce our work, consider two identical cold atoms approaching each other in the trap. If both atoms are in their ground state, the long-range attractive interaction is van der Waals as characterized by a C_6/R^6 potential. By contrast, if one of the atoms is in the excited state then a much longer range resonant-dipole interaction dominates as characterized by a C_3/R^3 potential. When considering the *total* angular momentum J available in the collision, it is important to realize that, because of the low kinetic energies of the atoms (i.e., the low temperature), there is a significant centrifugal (rotational) barrier $V_c(R)=\hbar^2J(J+1)/2\mu R^2$ that limits the available J states that can penetrate deep into the collision. At large internuclear separations, the van der Waals contribution can be neglected and the ground-ground potential is given approximately by $V_{gg}(R)=\hbar^2J(J+1)/2\mu R^2$. In general the barrier prevents high J states from participating. The classical cutoff in J occurs when $V_{gg}(R_{ex})\sim EK$ where $EK=\mu v_T^2/2=k_BT$. μ is the reduced mass, v_T is the thermal velocity, and T is temperature. We estimate the cutoff to be $J\leqslant J^{gg}_{\max}=[\sqrt{1+8k_BT\mu R^2/\hbar^2}-1]/2$. Here $J^{gg}_{\max}=12$ for the Na MOT with $T\sim T_D$ and $R=R_{ex}=800$ Å. For our trap laser detunings (small red detunings from the $3\,^2S_{1/2}+3\,^2P_{3/2}$ asymptote), the excited state molecular potential comes into resonance at $R_{ex}\sim 800$ Å . However, when excited-state collisions are considered, as in this work, it is more important to consider the classical J cutoff in the $S+P$ ground+excited state. The cutoff will be at a higher J value than for the ground+ground case because the rotational barrier is suppressed by the more attractive resonant-dipole interaction ($\sim C_3/R^3$). The effective ground+excited–state potential is approximately $V_{ge}(R)=-C_3/R^3+\hbar^2J^{ge}(J^{ge}+1)/2\mu R^2$. The maximum in this excited-state potential occurs when $dV_{ge}/dR=0$. The internuclear separation where the maximum in the potential occurs is $R_{\max}=3C_3/2\hbar^2J^{ge}(J^{ge}+1)$. In the excited state, the maximum allowed J is also obtained when $V_{ge}(R_{\max})\sim EK$. If we take $C_3=6.128$ a.u. [14] we obtain the significantly higher classical cutoff $J^{ge}_{\max}=22$ [15]. This is exactly where we observe a cutoff in our spectra.

The key result of our work is that the ground+excited state J levels observed in our experiment are populated in proportions set by a combination of the ground-state Boltzmann distribution for J^{gg} given a range of internuclear separations around R_{ex}. In our analysis we take account of the excitation probability and the selection rules for ΔJ for both the photoassociation step and the probe photon absorption step. In addition, we allow for a range of internuclear positions around R_{ex} at which the initial photoassociation step occurs (i.e., we allow for ''off-resonant excitation'' due to the natural linewidth of the transition, power broadening, etc.). This range can be large because the slope in the interaction potential $[\partial(V_e-V_g)/\partial R]$ is small near R_{ex}, an effect that further increases the range of ground+excited J levels that can be populated. Finally, to accurately fit our data we find that we must include the loss of (intermediate) excited-state population due to radiative decay. This effect is often referred to as ''survival'' and is particularly important for higher J states corresponding to excitation at larger internuclear separations R [5]. We stress that if any of these elements are left out of our semiclassical model, the quality of the fit is dramatically degraded. In the remainder of the paper we detail the treatment of the different contributions used in our analysis followed by our final results.

We begin by introducing our LE model in which the probability of populating a particular J state in the intermediate level is given by

$$P(J^{ge})=\frac{\int_\infty^{IT}P_{ex}(R_{ex})P_s(R_{ex},J^{ge})P_J^{gg}(R_{ex},J^{gg})dR_{ex}}{\sum_J\int_\infty^{IT}P_{ex}(R_{ex})P_s(R_{ex},J^{ge})P_J^{gg}(R_{ex},J^{gg})dR_{ex}}. \tag{1}$$

$P_{ex}(R_{ex})$ is the local equilibrium excitation rate at internuclear separation R_{ex}, $P_s(R_{ex},J^{ge})$ is the survival probability of molecules excited at R_{ex}, and $P_J^{gg}(R_{ex},J^{gg})$ is the local equilibrium probability for finding a particular total angular momentum J^{gg} at R_{ex}. IT is a judiciously chosen inner turning point discussed below.

At a given internuclear distance R, the available total angular momentum is characterized by a Boltzmann distribution: $P_J^{gg}(R,J^{gg})=(2J^{gg}+1)e^{-\hbar^2J^{gg}(J^{gg}+1)/2\mu R^2k_BT}/\Sigma_J(2J^{gg}+1)e^{-\hbar^2J^{gg}(J^{gg}+1)/2\mu R^2k_BT}$. Evaluating this expression shows that there is a large distribution of J values available at $R=R_{ex}\sim 800$ Å. In adopting the above expression for $P_J^{gg}(R,J^{gg})$ we have assumed that there is no optical pumping of the ground-state angular-momentum states via the excited states. This may not necessarily be true as the intensity of the laser increases and the Rabi frequency becomes large [16], as optical pumping may then populate higher J^{gg} states than included here.

The rate of excitation to optically active states is $P_{ex}(R_{ex})=\frac{1}{2}(I/I_0)/(I/I_0+\Delta_J^2/\Gamma_{mol}^2+\Gamma_{nr}^2/\Gamma_{mol}^2+1)$ where $\Delta_J=C_3/R^3-\hbar^2J^{ge}(J^{ge}+1)/2\mu R_{ex}^2+\hbar^2J^{gg}(J^{gg}+1)/2\mu R_{ex}^2$ is the local laser detuning from the potential energy surface [17,18], Γ_{mol} is the radiative decay rate, I_0 is the saturation intensity for the molecular transition, and Γ_{nr} is the nonradiative coupling between excited states [19].

We write the semiclassical survival probability $P_s(R_{ex},J^{ge})=e^{-\Gamma_{mol}\Delta t(R_{ex},J^{ge})}$ where $\Delta t(R_{ex},J^{ge})=t_{J^{ge}}-t_0$. t_0 is the time it takes the lowest J state (the orbital angular momentum s-wave) flux to propagate to an arbitrarily chosen point well inside the point where the ground-state s-wave collision contribution (here we focus on the partial wave) comes into resonance with the excited-state surface. Similarly, $t_{J^{ge}}$ is the time it takes the J^{ge} contribution to reach the above-mentioned point. $\Delta t(R_{ex},J^{ge})$ then is the differential time between the J^{ge}th and the s-wave classical arrival time at some point fairly deep in the collision. Since we are normalizing the amplitudes it is not necessary to calculate the full classical decay time. The difference in

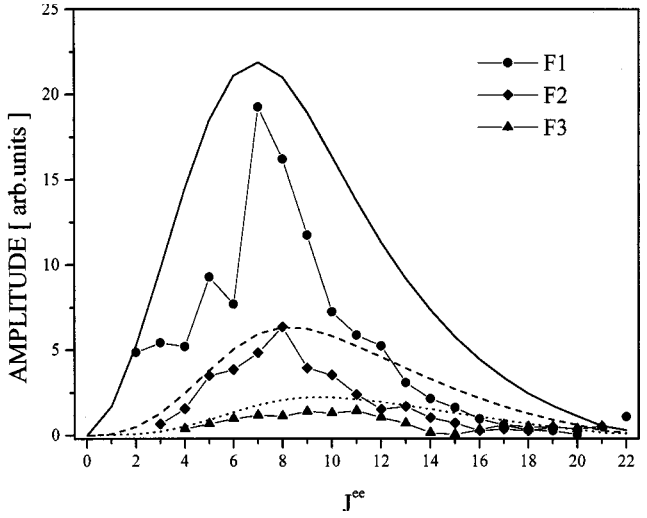

FIG. 2. The LE model for the normalized rotational amplitudes A_{F1}, A_{F2}, and A_{F3} as a function of angular-momentum quantum number. $Y=35$ for this plot. The rovibrational level $v_D-v=10.6$ where v is the rotational quantum number and v_D is the rotational quantum number at the dissociation limit.

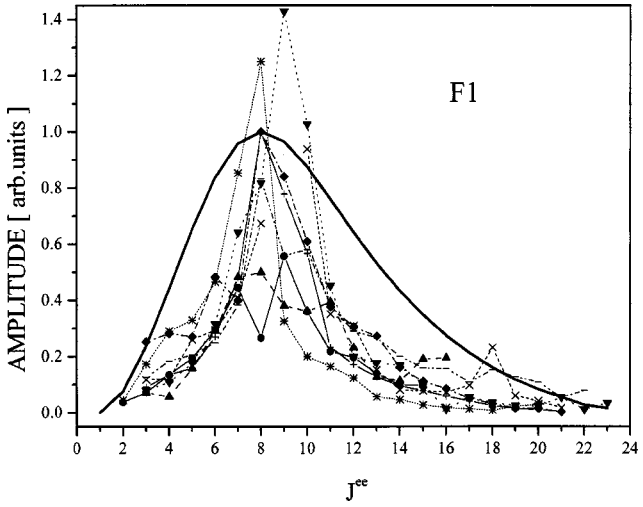

FIG. 3. A_{F1} from the LE model superposed on the experimental data for the $F1$ component. $Y=35$ throughout the curves.

survival time is mostly accumulated at long range where the time is determined by the thermal velocity and the rather small potential depth. We chose the inner point IT to be 100 Å since the s-wave excitation probability has decreased by over three orders of magnitude and the potential energy at the point is ~ 600 times the thermal energy. $t_{Jeg}=\int_{100}^{R_{ex}} dR/\sqrt{2/\mu(E_{k_i}-V(R))}$. The velocity on the excited-state potential is assumed to be set by T_D. Overall, this approach is an approximate way to include atomic motion and the Franck-Condon principle at the same time.

Our data are the amplitudes of lines in the $2\,^3\Pi_g$ rotational spectrum. Hence, it is necessary to modify expression (1) to account for the molecular excitation from the intermediate state to $2\,^3\Pi_g$. This is a well-known subject [20]. $2\,^3\Pi_g$ is best analyzed as intermediate between Hund's case (a) and (b) because of the small spin-orbit splitting near the $3\,^2S_{1/2}+3\,^2D_{1/2-3/2}$ atomic asymptote. We will assume that the excitation occurs out of the 0^+ component of $1\,^3\Pi_u$ [8]. In this case the relative intensities of the three components of $2\,^3\Pi_g$ denoted $F1$, $F2$, and $F3$ are

$$A_{F1}(J^{ee})=[J^{ee}P(J^{ee}+1)+(J^{ee}+1)P(J^{ee}-1)]S_{0,J^{ee}-1}/N,$$

$$A_{F2}(J^{ee})=[J^{ee}P(J^{ee}+1)+(J^{ee}+1)P(J^{ee}-1)]S_{0,J^{ee}}/N,$$

$$A_{F3}(J^{ee})=[J^{ee}P(J^{ee}+1)+(J^{ee}+1)P(J^{ee}-1)]S_{0,J^{ee}+1}/N,$$

respectively, where only transitions allowed by the selection rules $\Delta J=0,\pm 1(0\nrightarrow 0)$ are considered. $N=\Sigma J^{ee}[A_{F1}(J^{ee})+A_{F2}(J^{ee})+A_{F3}(J^{ee})]$. The $S_{i,j}$ are the standard elements of the transformation matrix from the intermediate coupling case to the Hund's case-(a) coupling case and may be found in [21]. These intensity expressions reflect the projection of the $2\,^3\Pi_{g(0)}$ component of $2\,^3\Pi_g$ onto each of the intermediate components [this is the case-(a) component that is optically coupled to the $2\,^3\Pi_{u(0)}$ intermediate component]. The only parameter in the $S_{i,j}$ is Y, which is the Hund's case-(a)-to-case-(b) recoupling parameter [20]. A plot of the normalized amplitude components for $Y=35$ is shown in Fig. 2. We stress that in our experiment, the J states populated in $2\,^3\Pi_g$ are determined by the rotational distribution in the intermediate state constrained only by the selection rule $\Delta J=0,\pm 1$.

The ratio of the amplitudes of the three different intermediate-state components fit $Y=35$ throughout the range of levels sampled ($v_D-v=7-15$). The normalized amplitudes from the experimental data for this interval are plotted along with the expected amplitude from expressions (2) in Figs. 3, 4, and 5. We emphasize that our fit has only one free parameter that represents an overall normalization scaling factor common to all three figures. The agreement with the simple LE model is quite good. It is also seen that

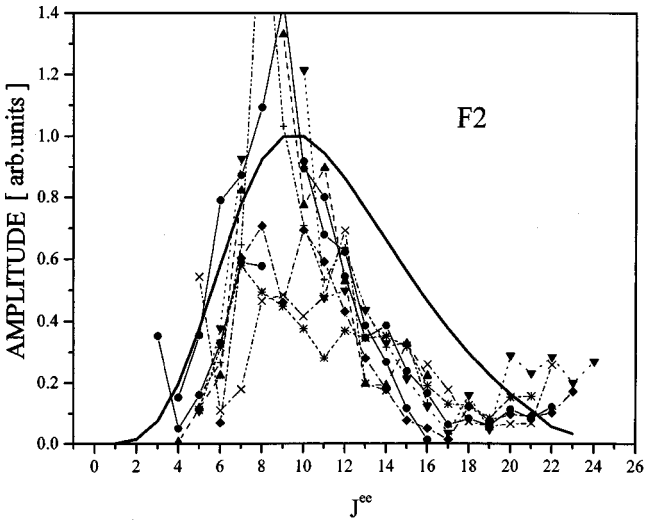

FIG. 4. A_{F2} from the LE model superposed on the experimental data for the $F1$ component. $Y=35$ throughout the curves. The amplitudes have been multiplied by a factor of 0.23 as compared to the $F1$ amplitudes.

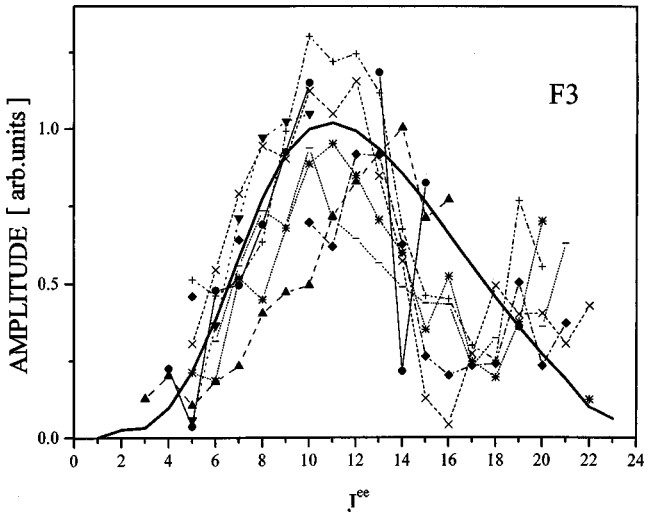

FIG. 5. A_{F3} from the LE model superposed on the experimental data for the $F1$ component. $Y=35$ throughout the curves. The amplitudes have been multiplied by a factor of 0.65 as compared to the $F1$ amplitudes.

the classical estimates of $J^{gg}_{\max}$ and $J^{ge}_{\max}$ are consistent with the model and the experimental data. It is interesting to note that, even though the experiment was done under conditions where $I/I_{sat}=15.5$ (I_{sat} is the atomic Na saturation intensity), the goodness of our fit implies that there is no evidence, within the experimental error, for optical pumping of high-angular-momentum states. This helps justify our LE model assumptions. In comparing expression (1) for $P(J^{ge})$ to the observed line amplitudes, we stress that we cannot adequately model our data unless we include (1) the effect of off-resonant excitation of large-angular-momentum states and (2) the effect of spontaneous decay, particularly for high J values.

In conclusion we have presented a direct measurement of the J states that take part in near dissociation limit ultracold optical collisions. The LE model we present agrees quite well with the experimental measurements, despite the deficiencies of this model noted in the literature [22]. This agreement suggests that excitation near the dissociation limit is inherently incoherent such that an effective averaging occurs and that the collision can be well described in the statistical limit. In addition, we have shown that by exciting the intermediate state to other higher-lying molecular states, useful information may be obtained about near dissociation limit optical collisions. This should be a useful approach because to date other spectra obtained near the $n\,^2S_{1/2}+n\,^2P_j$ state dissociation limit are complicated [13]. In the future it would be interesting to include the effects of hyperfine structure in our LE model.

We are grateful to O. Dulieu, P. Julienne, and W. Stwalley for valuable conversations. The authors would like to thank the National Science Foundation and the David and Lucille Packard Foundation for support. J.P. Shaffer would like to thank the Horton Foundation for financial support.

[1] J. Weiner *et al.*, Rev. Mod. Phys. **71**, 1 (1999), and references therein.
[2] D. Sesko *et al.*, Phys. Rev. Lett. **63**, 961 (1989); C. D. Wallace *et al.*, *ibid.* **69**, 897 (1992).
[3] A. Fioretti *et al.*, Phys. Rev. A **55**, R3999 (1997); J. Shaffer *et al.*, Eur. Phys. J. D **7**, 323 (1999).
[4] H. Wang *et al.*, Z. Phys. D: At., Mol. Clusters **36**, 317 (1996); P. D. Lett *et al.*, Annu. Rev. Phys. Chem. **46**, 423 (1995), and references therein.
[5] V. Sanchez-Villicanan *et al.*, Phys. Rev. A **54**, R3730 (1996); S. D. Gensemer and P. L. Gould, Phys. Rev. Lett. **80**, 936 (1998). For theoretical discussion of recycling physics, see Y. B. Band and P. S. Julienne, Phys. Rev. A **46**, 330 (1992); P. S. Julienne *et al.*, *ibid.* **49**, 3890 (1994); M. J. Holland *et al.*, Phys. Rev. Lett. **72**, 2367 (1994); Y. B. Band *et al.*, *ibid.* **50**, R2826 (1994).
[6] P. S. Julienne and J. Vigue, Phys. Rev. A **44**, 4464 (1991).
[7] D. Comparat *et al.*, J. Mol. Spectrosc. **195**, 229 (1999).
[8] J. P. Shaffer *et al.*, Phys. Rev. Lett. **83**, 3621 (1999).
[9] H. R. Thorsheim *et al.*, Phys. Rev. Lett. **58**, 2420 (1987).
[10] A. Gallagher and D. E. Pritchard, Phys. Rev. Lett. **63**, 957 (1989).
[11] E. L. Raab *et al.*, Phys. Rev. Lett. **59**, 2631 (1987).
[12] A. Cable *et al.*, Opt. Lett. **15**, 507 (1990).
[13] P. D. Lett *et al.*, Phys. Rev. Lett. **67**, 2139 (1991); P. S. Julienne and R. Heather, *ibid.* **67**, 2135 (1991).
[14] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995). More recent results on C_3 do not affect this calculation. See, for example, C. W. Oates *et al.*, Phys. Rev. Lett. **76**, 2866 (1996) or U. Volz *et al.*, *ibid.* **76**, 2861 (1996).
[15] By exciting at long range, we effectively circumvent the ground-state centrifugal barrier by ''climbing up and over'' the barrier using the excited-state potential.
[16] R. W. Heather and P. S. Julienne, Phys. Rev. A **47**, 1887 (1993).
[17] A. Gallagher, Phys. Rev. A **44**, 4249 (1991).
[18] R. Napolitano *et al.*, Phys. Rev. Lett. **73**, 1352 (1994).
[19] J. P. Shaffer *et al.*, Phys. Rev. A **61**, 011404 (2000); L. Marcassa *et al.*, *ibid.* **47**, R4563 (1993); P. D. Lett *et al.*, J. Phys. B **28**, 65 (1995). See also Refs. [5] and [6].
[20] G. Herzberg, *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules* (Krieger Publishing Co., Malabar, FL, 1989).
[21] I. Kovacs, *Rotational Structure in the Spectra of Diatomic Molecules* (Elsevier, New York, 1969).
[22] H. H. J. M. Boesten and B. J. Verhaar, Phys. Rev. A **49**, 4240 (1994). We believe that the successful use of a LE model in our work indicates that there is significant population mixing that occurs when there is long-range excitation and reexcitation, as is expected to occur in the MOT.