

Photoassociation of Cold Ca Atoms

Götz Zinner, Tomas Binnewies, and Fritz Riehle

Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany

Eberhard Tiemann

Institut für Quantenoptik, Universität Hannover, 30167 Hannover, Germany

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We present the first measurement of a photoassociative spectrum of an alkaline earth element near the dissociation limit. The observed spectrum of Ca_2 formed from cold atoms shows the regular vibrational series with the characteristic spacing of the $1/R^3$ asymptotic potential. The interpretation is in principle simplified compared to previous measurements on alkali metals by the nondegenerate ground state and the missing hyperfine structure of ^{40}Ca . As an example, we derive the natural decay rate of the excited atomic $4p\ ^1P_1$ state from the positions of the observed vibrational and rotational resonances with reduced uncertainty compared to previous measurements.

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The collision of two atoms with low relative velocity, a cold collision, within a light field gives the possibility to form a molecule. This process is called photoassociation. Photoassociative spectroscopy (PAS) using laser cooled atoms [1] proved to be a powerful tool for the determination of atomic properties such as excited state lifetimes in Na [2], K [3], Rb [4], or Li [5], ground state scattering lengths [4,6], and long range potentials, altogether opening the way to cold molecules. Most experiments were performed with alkali metals due to the convenient access to high densities and low temperatures in magneto-optical traps and due to the strong interest induced by the observation of Bose-Einstein condensates [7]. However, the quantitative analysis of the spectra often requires extensive calculations including atomic fine and hyperfine structure. In contrast, the most abundant isotopes of the alkaline earth metals show a nondegenerate ground state with no hyperfine splitting. Thus, thorough PAS studies have the potential to provide more accurate comparisons to theory. This advantage in the theoretical description is paid for by difficulties in the experimental observation of photoassociation, since the ensembles of laser cooled alkaline earth elements are usually less cold and less dense than those produced with alkali metals. This leads to a dramatically reduced signal strength and increases the demand on the sensitivity. Therefore, only little is known so far on photoassociation of alkaline earth metals. Recently, trap losses due to photoassociation were studied in a Sr magneto-optical trap [8] at a fixed very small detuning, and calculations on the photoassociative spectrum of cold Mg [9] showed that vibronic molecular structure should be observable near the dissociation limit. Recently, PAS was also realized in He_2^* [10], another simple system as compared to the alkaline metals, but with fine structure of the $^3S + ^3P$ atomic states.

In this Letter we present the first experimental investigation of the Ca_2 rovibrational spectra near the dissociation limit and compare the results with semiclassical and

full quantal calculations. The excitation ($\lambda = 423\text{ nm}$) of atomic pairs at large nuclear distances R leads to the formation of Ca_2 molecules predominantly in the $B\ ^1\Sigma_u^+$ excited state (Fig. 1). The dimer at the upper asymptote is bound by the resonant dipole-dipole interaction [11] according to

$$U(R) = D - C_3R^{-3}, \quad C_3 = \frac{3\hbar\lambda^3}{16\pi^3} \gamma. \quad (1)$$

D is the energy of the atomic asymptote $4s^2 + 4s4p$. The equation for the coupling constant C_3 depends on the wavelength λ and the spontaneous rate γ of the atomic transition $^1S_0\text{-}^1P_1$ and holds for the $^1\Sigma_u^+$ molecular state. Equation (1) is valid in an interval of R limited at small R by the onset of higher-order interactions, such as van der Waals terms and exchange interactions, and at large R ($R > \lambda/2\pi \approx 70\text{ nm}$) by retardation effects [12].

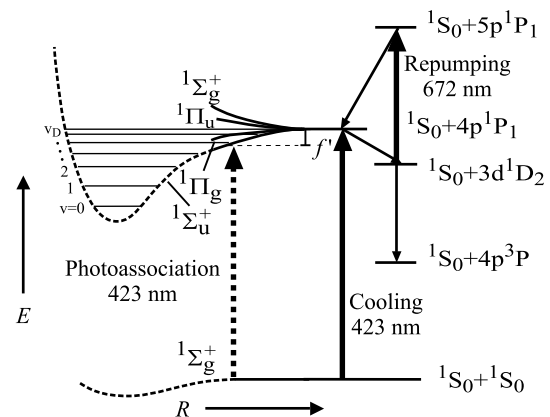


FIG. 1. Excerpt from the Ca_2 level scheme. Cooling and photoassociation utilize the dipole transition around $\lambda = 423\text{ nm}$. A repump laser ($\lambda = 672\text{ nm}$) prevents decay into metastable triplet levels via the 1D_2 state. Only the long-range part (solid line) of the $^1\Sigma_u^+$ molecular potential is probed in the experiment. The potential energies as a function of the internuclear distance R are indicated schematically. f' is the frequency difference between the photoassociation laser and the atomic resonance.

For rovibrational levels close to the atomic asymptote D the energies $E(v, J)$ can be derived by the WKB quantization, neglecting the above mentioned limitations [13].

$$E(v, J) = D - X_0(v_D - v)^6 + B_v J(J + 1), \quad (2)$$

$$X_0 = \left[\frac{\Gamma(4/3)}{2\sqrt{2\pi}\Gamma(5/6)} \right]^6 \frac{h^6}{\mu^3 C_3^2}.$$

In (2) v and J denote the vibrational and rotational quantum numbers of the excited state, respectively, v_D is an integration constant that can be interpreted as the hypothetical noninteger quantum number of the dissociation limit, and μ is the reduced mass of the diatomic molecule. The rotational constant B_v which is proportional to the inverse of the moment of inertia depends on the vibrational quantum number according to $B_v = X_1(v_D - v)^4$, where X_1 can be calculated in a similar way as X_0 [13]. Since the symmetry of the molecular ground state allows only even J values for spinless nuclei and $\Delta J = 0$ transitions are forbidden, only odd rotational quantum numbers are accessible via dipole transitions to the excited state. In the analysis of the experimental results we will count vibrational levels from the dissociation limit on with $v' = 1, 2, \dots$ giving $v_D - v = v' - 1 + (v_D \text{ modulo } 1)$ and $f' = D/h - f_L$ with resonances at $f'_{v'} = E(v', J)/h$ where f_L is the frequency of the laser.

We detect the photoassociation by observing the reduction of the number of magneto-optical trapped calcium atoms in the presence of the photoassociation laser. The excited molecules may escape from the trap either by spontaneous decay to the molecular ground state (radiative escape) or by state changing collisions (SC) at small internuclear distances where the bound state may couple to unbound states of other electronic configurations. The resulting atomic pair can acquire enough kinetic energy to leave the shallow trap (depth ≈ 3 K). The loss rate βn^2 of atoms from the trap due to photoassociative collisions is proportional to the square of the atomic density n inside the trap. The parameter β depends linearly on the intensity of the photoassociation laser only as long as saturation effects can be neglected. Furthermore, β depends on the detuning f' of the photoassociation laser. Quantum calculations for Mg [9] and classical calculations for Sr [8] show that β should be in the range of $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at an intensity of 1 mW/cm^2 and detunings larger than 1 GHz . For Sr the calculations were experimentally checked for a detuning of 56 MHz [8].

The measurements were performed in a magneto-optical trap, operating on the $^1S_0 - ^1P_1$ transition at 422.79 nm (see Fig. 1), and filled directly from a thermal atomic beam. To close the leak from the cooling transition via the 1D_2 state we used a repump technique similar to [14] on the transition to the $4s5p \ ^1P_1$ state ($\lambda = 672 \text{ nm}$). With the repump laser on, the lifetime of the trap reached $\tau = 50 \text{ ms}$ and was limited by residual gas in the vacuum chamber (some 10^{-5} Pa). The radius r and density n_0

of the trapped ensemble were determined by absorption imaging on the cooling transition leading to typical values of $r = 0.5 \text{ mm}$ and $n_0 = 2 \times 10^{10} \text{ cm}^{-3}$. The temperature of the ensemble was deduced independently from the ballistic expansion of the cloud and from the Doppler width of the excitation spectrum on the $^1S_0 - ^3P_1$ intercombination line, yielding $T = 3 \text{ mK}$. Further details on the apparatus are described in [15].

To induce photoassociative trap losses we applied a standing wave from another laser red detuned by f' from the atomic resonance to the ensemble. This beam was switched on and off for time intervals of 100 ms . During this time, the number of trapped atoms settled to the steady-state values with and without photoassociative losses, respectively. The intensity of the photoassociation beam was up to $I = 5 \text{ W/cm}^2$. The trap population was measured by recording the fluorescence induced by short pulses (0.1 ms) of light resonant with the cooling transition before and after each interaction period with the photoassociation laser. We used a resonant probe beam to reduce the sensitivity to laser frequency fluctuations, thus improving the signal-to-noise ratio. The collisional loss fraction is the ratio of the signal reduction due to the photoassociation and the signal obtained without photoassociation. The detuning of the laser with respect to the atomic resonance was determined by measuring its beat frequency with the frequency stabilized trapping laser which was set to 57 MHz below the resonance. For each detuning we averaged several hundred measurement cycles, leading to an observation time of a few minutes per point.

The spectrum of Fig. 2 is composed of several scans in selected small windows up to detunings of nearly 30 GHz with a series of well-resolved resonances. Since the data were taken during several weeks, the resulting day-to-day

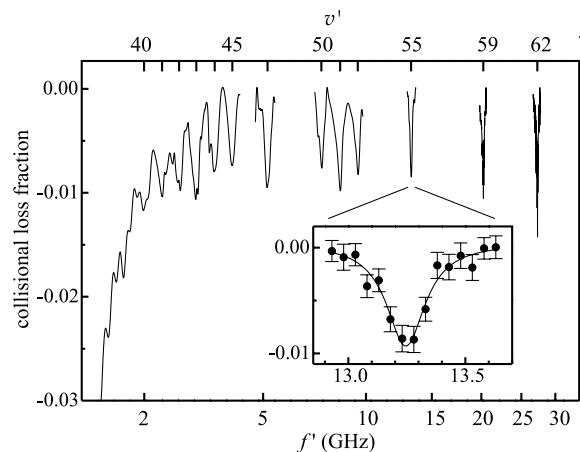


FIG. 2. Measured vibronic spectrum at the asymptote of the $B^1\Sigma_u^+$ branch of Ca_2 . The plot shows the relative reduction of the trap population versus the detuning of the photoassociation laser. The frequency scale is proportional $\sqrt[6]{f'_{v'}}$ to give equally spaced vibrational levels. The inset shows an enlarged view of a typical resonance ($v' = 55$).

variations of the baseline are removed to avoid misinterpretation of the data. The relative intensities of the vibrational lines are influenced by different atomic density and laser power of the composed scans. The drop towards small detunings ($f' < 2$ GHz) is due to the resonant interaction of the photoassociation beam with single atoms, which are pushed out of the trap by radiation pressure.

The inset in Fig. 2 shows an enlarged view of a typical line shape. The observed signal-to-noise ratio did not allow detection of asymmetries due to the energy distribution of the ground state atoms [16]. The rotational structure was partially resolved for the ($v' = 59$) and the ($v' = 62$) line. The other vibrational lines appear to be symmetrical at the current level of accuracy with a FWHM of approximately 200 MHz. We interpret this line width as being due to the combined influence of the natural molecular line width ($2\Gamma \approx 70$ MHz), the thermal broadening (≈ 60 MHz at 3 mK), and the unresolved rotational structure. The loss at the center of a resonance is typically 1% yielding $\beta = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ($I = 5 \text{ W/cm}^2$) using the trap loading equation [8] with the measured parameters ($\tau = 50$ ms, $n_0 = 2 \times 10^{10} \text{ cm}^{-3}$).

Because of this unexpected low value of β [8,9] the laser intensity had to be chosen well above the atomic saturation intensity ($I \approx 40I_{\text{sat}}$) to observe the small photoassociative losses. The effective saturation intensity for photoassociation is known to be higher than the atomic saturation intensity [17]; however, our present data do not allow a decision whether saturation effects influence the signal strength and the linewidth in our experiment.

In total, the center frequencies of 13 vibrational levels have been identified in the spectrum. These values allow the determination of X_0 and hence γ . To get accurate values we have corrected for line shifts due to the unresolved rotational structure and to the thermal energy distribution of the ground state atoms. We estimated the thermal shift to be -50 (22) MHz [18], independent of v and J [19,20]. The influence of the rotational splitting was deduced from the partially resolved rotational lines for $v' = 59, 62$. The measured spectrum of the ($v' = 62$) line (Fig. 3) can be decomposed into four rotational sublines. Since the rotational energies of a Ca atomic pair at a distance of $R = 10$ nm (a typical classical turning point of the observed vibrational levels) correspond to temperatures of 0.7 mK, 2.4 mK, and 5.1 mK for $J = 2, 4$, and 6, the number of observed sublines is compatible with the measured temperature of 3 mK. The observed linewidth is close to 130 MHz as expected from the convolution of the natural and thermal profiles, neglecting saturation effects. The rotational splitting is described by $B_{62}J(J+1)$ with $B_{62}/h = 8.36(50)$ MHz. The corresponding result for the ($v' = 59$) line gives $B_{59}/h = 6.38(70)$ MHz. To correct for the rotational shift at smaller v' , we assumed that $B_{v'} = X_1 v'^4$ and determined $X_1/h = 0.565(35)$ Hz from the two measured values and assumed that the peaks of the rotationally unresolved lines correspond to $J = 3$.

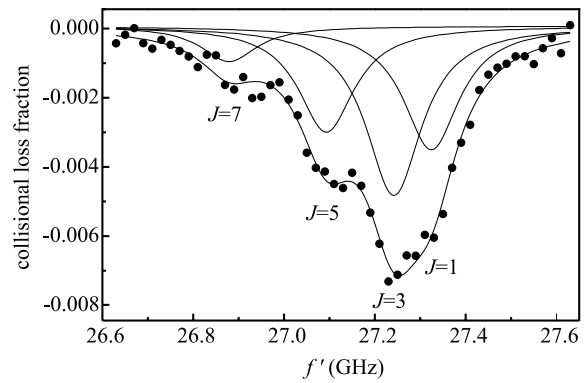


FIG. 3. Vibrational ($v' = 62$) line with four resolved rotational lines corresponding to $J = 1, 3, 5$, and 7, respectively. The width of the individual lines is 150 MHz.

Figure 4 shows the values of the observed resonances and a fit according to (2), including the above mentioned corrections, with X_0 and the fractional part of v_D being the fit parameters. From the fit we derive the vibrational constant to be $X_0/h = 0.488(6)$ Hz and the fractional part of v_D to be 0.83. The residuals show no systematic deviation from the v'^6 law, indicating that all lines stem from a single molecular state bound by a potential proportional to R^{-3} in the investigated region.

Assuming that we have excited the $^1\Sigma_u^+$ state, this leads to an atomic decay rate of $\gamma = 2.182(12) \times 10^8 \text{ s}^{-1}$, which is in good agreement with the value of $\gamma = 2.174(95) \times 10^8 \text{ s}^{-1}$ determined by level crossing experiments [21].

To check the validity of the semiclassical approach [Eq. (2)] for deriving the constant X_0 we applied a full quantal analysis with the asymptotic potential according

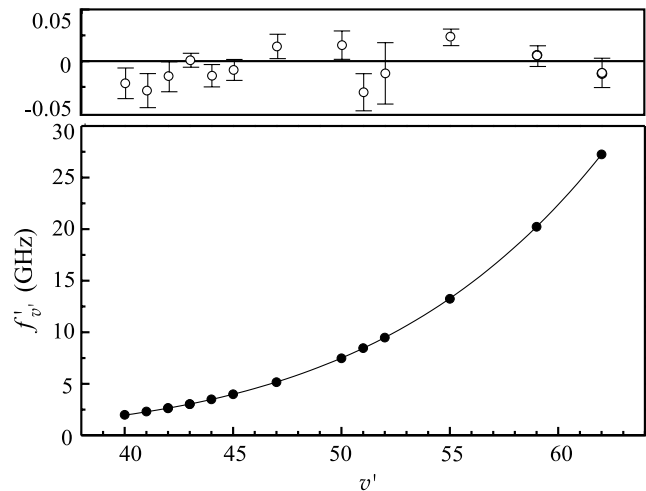


FIG. 4. Frequency difference $f'_{v'}$ from the asymptote of the measured vibrational levels versus their quantum number v' . $f'_{v'}$ is proportional v'^6 (solid curve). The residuals are plotted in the upper panel with the error bars indicating only the statistical uncertainty.

to (1). Searching for eigenstates with such potential we followed an idea of Moerdijk *et al.* [22] applied in the analysis of the photoassociation spectrum of Rb [4] and replaced the boundary condition for the wave function at small internuclear distance by an almost constant phase in the inner part of the classically allowed interval for the high lying vibrational states. The Schrödinger equation was solved numerically and the fit of all observed levels including rotational energy varies the coefficient C_3 and the phase modulo π . Changing the internuclear distance from 0.6 to 1.5 nm for the phase reference used as inner boundary condition, sufficiently far from the outer turning points of the vibrational levels, the fit gives stable values for $C_3 = 0.535(3) \times 10^3 \text{ nm}^3 \times \text{cm}^{-1} = 16.5(1)$ a.u. and thus a rate of $\gamma = 2.205(8) \times 10^8 \text{ s}^{-1}$. This result is in agreement (2σ) with the WKB approximation and confirms the simple semiclassical approach. With the quantum method it is easy to check the influence of higher order dispersion terms in the potential. Introducing C_6 within reasonable limits the derived C_3 stays completely in the error interval of the value given above, which is consistent with the fact that the outer turning point of the deepest observed level $v' = 62$ is at 8.4 nm.

In conclusion, we presented the first observation of a photoassociative spectrum of ^{40}Ca near an asymptote. Its simple atomic structure makes ^{40}Ca , as other alkaline earth elements, an ideal testing ground for theories on photoassociative collisions. We derived the lifetime of the atomic $4s4p \ ^1P_1$ state with an uncertainty, which is reduced by more than a factor of 5 compared to previous measurements. Since the uncertainty is limited by the assumed line profile, future measurement of fully resolved rotational structure will allow us to reduce this uncertainty significantly. The analysis of the data required only a single term of the long-range interatomic potential and no knowledge on its inner part. Our results demonstrate that photoassociative spectroscopy can be as fruitful for alkaline earths as it turned out to be for the alkali metals. Apart from lifetime measurements, a detailed understanding of ultracold collisions is essential for the next generation of ultraprecise clocks and frequency standards. In addition, it will enable the determination of the s -wave scattering length for ground state atoms, which is a critical parameter for the feasibility of Bose-Einstein condensates. With the availability of new cooling techniques [23] the required phase space densities come within reach for alkaline earth metals. With such new experiments the reliable determination of the scattering length for cold Ca and other alkaline earth metals seems necessary and is possible using photoassociative spectroscopy.

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