# Formation of Cold $Cs_2$ Molecules through Photoassociation

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We have performed photoassociative spectroscopy of cold Cs atoms in a vapor-cell magneto-optical trap, within 10 $\mathrm{cm}^{-1}$ below the dissociation limit $6s\,^2S_{1/2} + 6p\,^2P_{3/2}$. Our detection method is based on pulsed-laser photoionization of $Cs_2$ molecules, selectively detected through a time-of-flight mass spectrometer. Temporal and spatial analysis of $Cs_2^+$ ions show for the first time the formation of translationally cold $Cs_2$ triplet ground state molecules, at a temperature $T \sim 300\ \mu$K. [S0031-9007(98)06137-7]

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In the past decade the ability to make cold atomic samples has allowed researchers to explore many fascinating new phenomena, including atomic interferometry, atomic fountains, photoassociation (PA), and Bose-Einstein condensation. In view of the possibilities offered by cold atoms, it is not surprising that the idea of making cold molecules has been explored. However, in contrast to atoms, laser cooling of molecules is very difficult [1] because of the lack of a closed two-level optical pumping scheme for recycling population. The formation of translationally cold ground state molecules after spontaneous deexcitation of photoassociated molecules [2] appears to be easier, but, unfortunately, this process is generally quenched by the spontaneous emission that leads back to the dissociation of the transient cold molecule into two free atoms. More complex schemes have been proposed [3].

Molecular photoassociative spectroscopy of cold alkali atoms has opened the way to the observation of long-range dimers [2] and to the determination of long range potential curves. Up to now, PA has been demonstrated for all alkali atoms [4] except cesium. Moreover, PA experiments have allowed one to probe the ground state of $Li_2$ [5], $Na_2$ [6], and $Rb_2$ [7] and to determine the scattering lengths necessary to predict the stability of the condensate. The lack of experimental data for $Cs_2$ is particularly disturbing in view of the prominent role of this element in metrology and of the realization of a cesium condensate.

In this Letter, we report the first observation of molecular PA of cold cesium atoms below the dissociation limit $6s\,^2S_{1/2} + 6p\,^2P_{3/2}$, and the first observation of translationally cold $Cs_2$ molecules in their triplet ground state. A pair of ground state cold Cs atoms is resonantly excited to a $0_g^-$ rovibrational state of $Cs_2$ using a cw PA laser. A significant fraction of these photoassociated molecules decay to bound levels of the $^3\Sigma_u^+$ ground state, yielding long lived translationally cold molecules. The latter are detected by pulsed laser ionization into $Cs_2^+$ ions, through a time of flight mass selection. The paper is organized in the following way. First we describe our experimental approach and the results which show clearly that cold $Cs_2$ molecules are found. Then we describe the $Cs_2$ molecular properties that can be deduced from experimental spectrum and explain why cesium is a particularly favorable case for cold molecules formation. Finally, the intensity minimum in the spectral lines is analyzed in terms of the scattering length.

The principle of the experiment is simple. We illuminate the trapped, cold Cs atoms with a cw laser to produce the photoassociative transitions [see Fig. 1(a)]:

$$\mathrm{Cs}(6s) + \mathrm{Cs}(6s) + h\nu_1 \rightarrow \mathrm{Cs}_2[\Omega_{g,u}(6s6p\,^2P_{3/2}; v, J)]\,.$$

The experimental setup has been partly described in a previous Letter [8]. The vapor-cell magneto-optical trap (MOT) can load up to $5 \times 10^7$ atoms at a peak density of the order of $10^{11}\ \mathrm{cm}^{-3}$, with an estimated temperature of the order of 200 $\mu$K [9]. Cooling and Repumping lasers, respectively, tuned 13 MHz to the red of the $6s\,^2S_{1/2}(F = 4) \rightarrow 6p\,^2P_{3/2}(F' = 5)$ and resonant with the $6s\,^2S_{1/2}(F = 3) \rightarrow 6p\,^2P_{3/2}(F' = 4)$ atomic transitions, keep atoms cycling between the $6s\,^2S_{1/2}(F = 4)$ ground state and the $^2P_{3/2}(F' = 5)$ excited state. The cold atoms are illuminated by the beam of a PA diode laser (SDL 5712-H1, 100 mW, $\lambda_1 \sim 852$ nm) focused on a diameter of roughly 200 $\mu$m, leading to an available intensity in the MOT zone of nearly 200 $\mathrm{W\,cm}^{-2}$. Its frequency $\nu_1$ is scanned over a 300 GHz range on the red of the cooling transition by slowly varying the diode temperature. This technique permits us to scan the whole range without any laser-mode jump. The frequency scale has been calibrated by using the Cs saturated absorption lines, a Fabry-Pérot interferometer, and the absorption lines of iodine.

$Cs^+$ and $Cs_2^+$ ions are produced by a pulsed dye laser (7 ns, 1 mJ, focused to a 1 $\mathrm{mm}^2$ spot) pumped by the second or third harmonic of a Nd-YAG laser, running at a 10 Hz repetition rate, and tunable on the range $\lambda_2 \sim$ 500–750 nm. After the laser pulse, a pulsed high voltage field (4 kV, 0.5 $\mu$s) is applied at the trap position by means of a pair of grids spaced 15 mm apart. The ions are expelled from the interaction region in a 6 cm free field zone constituting a time-of-flight mass spectrometer

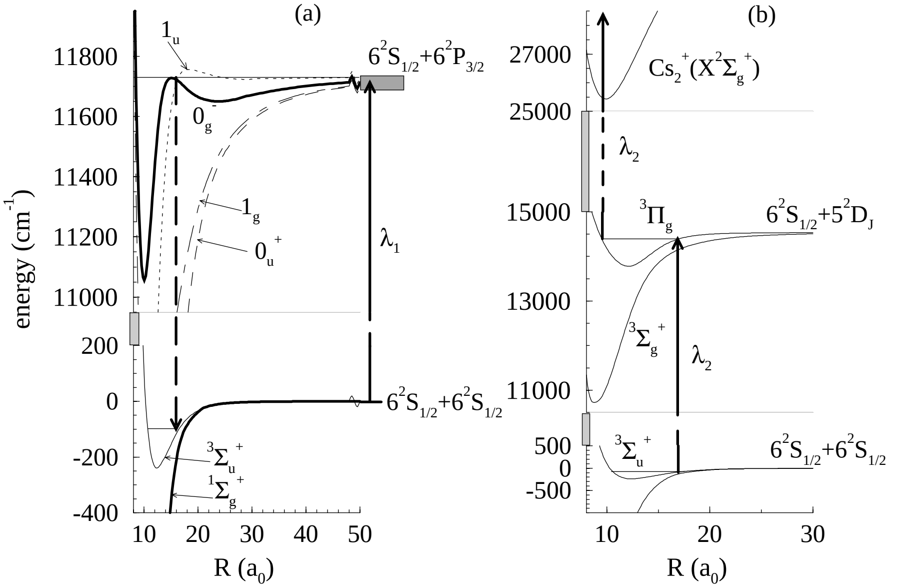

FIG. 1. (a) Diagram of the $Cs_2$ optical transitions and molecular states relevant for the photoassociation experiment. (b) Two-step ionization scheme for the $Cs_2^+$ detection. All potential curves are determined from Refs. [11,12].

which separates $Cs_2^+$ from $Cs^+$ ions, and detected by a pair of microchannel plates. In these conditions, the two ion signals last typically about 100 ns, have respective arrival times of 1.9 $\mu$s and 1.3 $\mu$s, and can easily be independently recorded with gate integrators. The relative magnitude of the $Cs^+$ and $Cs_2^+$ depends strongly on the pulsed laser wavelength and intensity. In particular, the $Cs_2^+$ signal depends linearly on intensity, while the $Cs^+$ one is quadratic. The latter is mostly due to two-photon ionization of atomic cesium in the $6p\,^2P_{3/2}(F' = 5)$ excited state and is dramatically reduced if the trapping laser is switched off before the laser pulse, leaving all atoms in the $6s\,^2S_{1/2}(F = 4)$ ground state.

In Fig. 2 we show a typical photoassociation spectrum, obtained from $Cs_2^+$ signal and for $\lambda_2 \sim 716$ nm. No corresponding resonances on the $Cs^+$ ion signal are observed. We notice that a $Cs_2^+$ ion signal is observed even without the PA laser. We interpret this fact supposing that the cooling and repumping lasers already produce molecular photoassociation. In order to suppress this background, we have switched off all the cw lasers (cooling, repumping, and photoassociating), for a time interval before shooting the ionizing pulse. We observe that the $Cs_2^+$ ion signal is still present and decreases, as a function of the delay, with a characteristic time of nearly 6 ms. This time is 5 orders of magnitude larger than the radiative lifetime of any singly excited molecular state with electric-dipole allowed transition to the ground state. Indeed, it is of the order of the time during which atoms and molecules move significantly out of the trap because of their ballistic expansion in gravity. Analogously, we observe that switching on the PA laser, tuned on a given resonance line of the experimental spectrum, and delaying the pulsed laser produce a $Cs_2^+$ ion signal which increases with the delay and reaches a constant value in about 3 ms. These two results clearly indicate that the $Cs_2^+$ ions are not produced by direct photoionization of the excited rovibrational molecular levels, but by photoionization of ground state molecules.

We have analyzed the fall of the atomic and molecular clouds by horizontally space scanning the pulsed laser beam (tightly focused on a round spot of 0.3 mm diameter) at different distances below the MOT while keeping all the cw (trapping, repumping, and PA) lasers on. We observe the disappearance of the $Cs^+$ ion signal coming from the MOT (a small signal due to ionization of the background

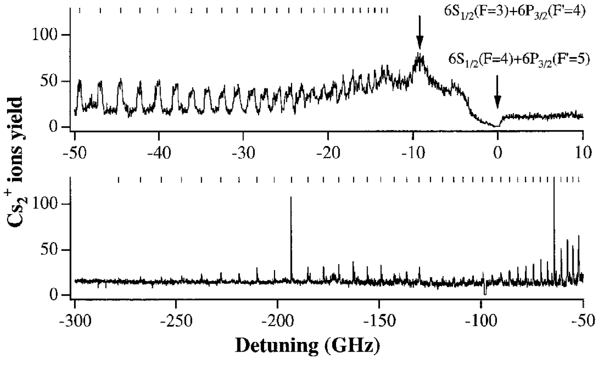

FIG. 2. $Cs_2^+$ ion signal versus the detuning of the PA laser. The assigned positions of the vibrational levels are indicated by small bars. The PA laser step is 30 MHz and ion counts are averaged on 10 laser pulses. The zero of counts is given at $\Delta = 0$ and $\Delta = -100$ GHz, where the MOT is off. Note that the first dissociation limit does not correspond to any atomic transition; the second one corresponds to the $6s\,^2S_{1/2}(F = 4) \rightarrow 6p\,^2P_{3/2}(F' = 5)$ transition.

Cs gas is still present), while the $Cs_2^+$ ion signal is still present and spatially spread out (see Fig. 3). Analysis of these data gives an average transverse velocity of 13 cm/s (with a 30% error bar), corresponding to a temperature of the initial cold molecular cloud of the order of 300 $\mu$K, i.e., close to the estimated temperature of the trapped atomic sample.

In the spectrum of Fig. 2, we identify the energy $E(v)$ of 63 lines regularly spaced, plus 2 very narrow "giant lines." We have assigned the energies of the first series to a single vibrational progression, corresponding to an outer well in the $0_g^-$ potential curve, correlated to the $6s\,^2S_{1/2} + 6p\,^2P_{3/2}$ dissociation limit. As in the vicinity of this limit the potential curves are expected to behave as $-C_3/R^3$, it is usual to identify the symmetry by fitting $E(v)$ to the analytic Le Roy–Bernstein (LRB) law [10]. The fitted value is $C_3^{\mathrm{fit}} = 12.1 \pm 0.2$ a.u. Four attractive long-range Hund's case (c) states can be populated: $1g$, $0_u^+$, $0_g^-$, and $1_u$ (transition from the ground state to the attractive $2_u$ state is electric-dipole forbidden). Their corresponding dipole-dipole asymptotic coefficients $C_3^{\mathrm{eff}}$, computed from nonrelativistic calculations of Ref. [11], are, respectively, 17.46, 16.22, 10.47, and 2.25 a.u. Our fitted value is in agreement with none of these predictions, but differs by 15% from the expected $0_g^-$ value. We interpret the discrepancy between the value of $C_3^{\mathrm{fit}}$ and the theoretical $C_3^{\mathrm{eff}}$ as due to the particular structure of the $0_g^-$ curve of the cesium dimer, which makes a simple LRB model too crude. This is illustrated in Fig. 1(a), where we display the double well structure obtained by matching at $R = 28a_0$ ($a_0$: Bohr radius), the asymptotic curve deduced from Ref. [11], with the short and intermediate range $0_g^-$ curve deduced by diagonalizing the atomic fine-structure Hamiltonian within the subspaces of the accurate $^3\Sigma_g^+$ and $^3\Pi_g$ *ab initio* potential curves of Ref. [12]. The outer well (bottom: $R = 24a_0$, $D_e = 83\ \mathrm{cm}^{-1}$) is separated from the inner well by a bump located at $15a_0$, and close in energy to the dissociation limit. The energies of the calculated bound levels reproduce reasonably the progression of the experimental ones. This double well structure, with its intermediate bump, provides thus an excellent explanation for the formation of cold molecules, due to the favorable Franck-Condon (FC) transition to the $^3\Sigma_u^+$ bound states. Moreover, by computing the adiabatic asymptotic potential curves including the atomic hyperfine interaction, we predict, in the central part of the energy range explored by the experiment, a linewidth due to the hyperfine structure of about 6, 1.5, 0.6, and 6 GHz for the $1_g$, $0_u^+$, $0_g^-$, and $1_u$, respectively. As the rotational structure is expected to be small ($\leq$20 MHz), we assign the observed width of the peaks to the hyperfine structure. All these arguments make us definitely assign the observed series to the $0_g^-$ state.

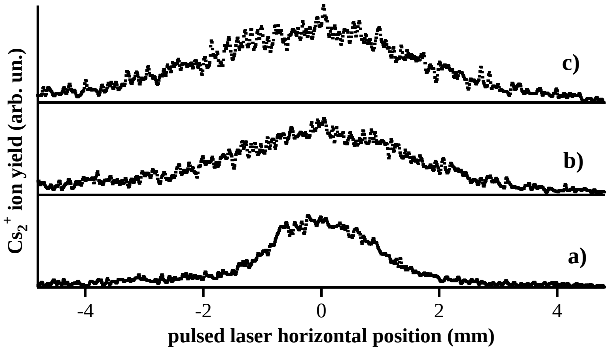

FIG. 3. Spatial analysis of the molecular density by varying the ionizing laser horizontal position: (a) At the MOT position, (b) 1.3 mm below, and (c) 2.1 mm below.

The two giant lines at $-64$ and $-193$ GHz are interpreted as two bound levels of the inner well, populated by tunneling through the barrier. Their extremely large intensity is due to a much better FC overlap with the $^3\Sigma_u^+$ states than the levels of the $0_g^-$ states of the external well.

Finally, in the spectrum we observe a modulation of the line intensities, with a minimum at a detuning $\Delta_1 = -114 \pm 2$ GHz that does not depend on the ionizing laser wavelength $\lambda_2$. We interpret this feature as being due to the FC factors resulting from the transitions between the initial state $\Psi(R;E)$, corresponding to two cold free atoms, and the final rovibrational levels of the $0_g^-$ state, with energy $D - h\Delta_0$, where $D$ is the dissociation energy. As discussed in [13], the overlap integral is roughly proportional to $\Psi(R_0;E)$, where $R_0$ is the classical outer turning point of the excited rovibrational wave function. The existence of a minimum in the excitation at $\Delta_1$ reflects the presence of a node in the ground state $s$-wave wave function at the position $R_1$. The position of the last nodes of the $s$ wave can be determined as a function of the scattering length $a$ (see Fig. 4 and Appendix A in Ref. [6]). From the experimental data and the adiabatic potential curves we get $R_1 = (83.8 \pm 2)a_0$. This value is interpreted as being the position of either the last node of the $s$-wave wave function, implying a large negative value of $a$, or the second last node, implying a large positive value of $a$. This scattering length value characterizes the dissociation channels which are involved in the experiment, i.e., the $(F_1 = 4, F_2 = 4, F_{\mathrm{tot}}, M_{\mathrm{tot}})$ diatomic states with any $(F_{\mathrm{tot}}, M_{\mathrm{tot}})$ value, where $(F_{\mathrm{tot}} = F_1 + F_2)$. These channels are all adiabatically connected to the triplet potential. This preliminary result is compatible with Ref. [14], where the absolute value of the triplet state scattering length is found to be larger than $260a_0$.

We cross-checked our interpretation of the ionization process by keeping $\lambda_1$ fixed and scanning the wavelength $\lambda_2$ of the pulsed laser in most of the 500–750 nm range. While we observe a very weak $Cs_2^+$ ion signal for most wavelengths, we get two windows of a few hundred wave numbers around $\lambda_2 \sim 716$ and 554 nm for which the signal is much larger, for any fixed $\lambda_1$. These ionization regions correspond to a two-step ionization via

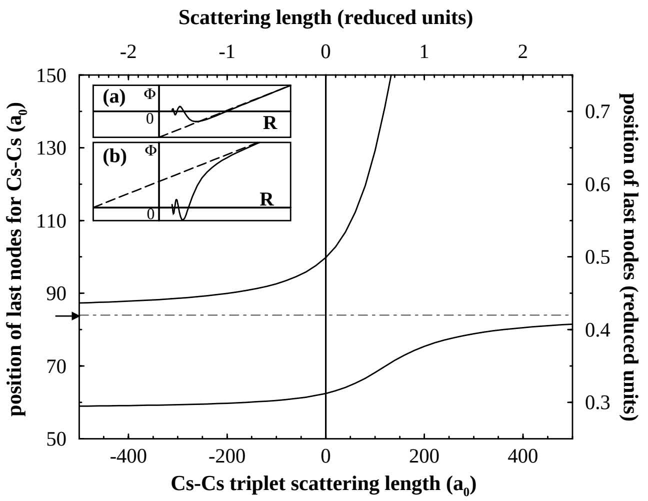

FIG. 4. Position of the last two nodes of the solutions, with asymptotic behavior $(x - l)$, of the differential equation $y'' + y/x^6 = 0$, versus the parameter $l$. For any atom, the node position is given by $R_k = \alpha x_k$ and the scattering length by $a = l/\alpha$, $\alpha = (2\mu C_6/\hbar^2)^{1/4}$ being a scaling factor. Left and bottom scales are in atomic units; right and top scales are in reduced units. The arrow indicates the position deduced from the experimental spectrum. Insets (a) and (b) show the last nodes of the $s$ wave functions for a positive $(l = 1)$ and a negative $(l = -1)$ scattering length.

the intermediate vibrational levels $\Omega_g(6s5d\,^2D_{3/2,5/2})$ and $\Omega_g(6s7s\,^2S_{1/2})$ [see Fig. 1(b)]. The presence of the intermediate state explains also the linear dependence of the $Cs_2^+$ signal on the pulsed laser intensity. It is interesting to notice that the wavelength $\lambda_2 = 716$ nm also corresponds to the transition $Cs_2[\Omega_{g,u}(6s6p\,^2P_{3/2}; v, J)] \rightarrow Cs_2^+[X^2\Sigma_g^+(v = 0, 1, 2)]$. Yet, as demonstrated above, the contribution of such a direct ionization process to the signal is not observed at the explored wavelength $\lambda_2$. We thus conclude that photoassociated molecules are stabilized by spontaneous emission from the $0_g^-(6s6p\,^2P_{3/2}; v, J)$ level towards the $^3\Sigma_u^+(6s6s\,^2S_{1/2}; v', J')$ ground state, and then photoionized.

In conclusion, we have reported for the first time the PA spectroscopy of Cs cold atoms by using a pulsed laser ionization detection. The experimental spectrum differs noticeably from spectra obtained for other alkali dimers, where three series $0_g^-$, $0_u^+$, and $1_g$ are usually observed. This result is interpreted as a consequence of the intermediate Condon point provided by the double-well shape of the $0_g^-$ potential, which is responsible for the existence of a rather efficient channel in spontaneous emission for the creation of triplet ground state molecules. PA of Cs cold atoms is thus a favorable case for the formation of translationally cold molecules which have been observed here for the first time. The temperature of the molecular cold sample is found to be approximately equal to that of the initial atomic sample. We do not expect our molecular sample to be vibrationally cold. Preliminary calculations show that the spontaneous emission populates most of the $^3\Sigma_u^+$ ground state vibrational levels with $v \geq 8$. The number of molecules detected per laser pulse does not exceed a few hundred. Possible ways to increase this number should be to use a higher power Ti:sapphire laser and to stimulate the emission towards selected vibrational levels of the ground triplet potential. Our PA experiment should open a way to the physics of cold molecules. In the future, dipolar or magnetic traps could be developed to store these molecules.

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